Engineering

VOLUME 30 JULY-AUGUST 1952 NUMBERS 7 and 8

Canadian Journal of Technology

Editor: G. A. LEDINGHAM

Published by THE NATIONAL RESEARCH COUNCIL
OTTAWA CANADA

CANADIAN JOURNAL OF TECHNOLOGY

(Formerly Section F, Canadian Journal of Research)

The CANADIAN JOURNAL OF TECHNOLOGY is published monthly by the National Research Council of Canada under the authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. Matters of general policy are the responsibility of a joint Editorial Board consisting of members of the National Research Council of Canada and the Royal Society of Canada.

The National Research Council of Canada publishes also: *Canadian Journal of Botany, Canadian Journal of Chemistry, Canadian Journal of Medical Sciences, Canadian Journal of Physics, Canadian Journal of Zoology.*

The CANADIAN JOURNAL OF TECHNOLOGY and the CANADIAN JOURNAL OF CHEMISTRY have been chosen by the Chemical Institute of Canada as its medium of publication for scientific papers.

EDITORIAL BOARD

Manuscripts should be addressed to:

DR. LÉO MARION,
Editor-in-Chief,
Canadian Journal of Technology,
National Research Council,
Ottawa, Canada.

Each manuscript should be typewritten, double-spaced, and the original and one extra copy submitted (see **Notice to Contributors** inside of back cover).

Subscriptions, renewals, and orders for back numbers should be addressed to:

Administrative Services,
National Research Council,
Ottawa, Canada.

Subscription rate: $4.00 a year; single numbers: 50 cents. Special rates can be obtained for subscriptions to more than one of the Journals published by the National Research Council.

earch
uncil
of a
and

tany,
al of

have
ntific

ction
II

ction
V

A

extra

ed for
uncil.

Canadian Journal of Technology

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOLUME 30 | JULY-AUGUST, 1952 | NUMBERS 7 and 8

ASSESSMENT OF THE FRITZ CONTINUOUS BUTTER-MAKING MACHINE FOR CANADIAN USE[1]

BY J. A. PEARCE,[2] DYSON ROSE, AND H. TESSIER

ABSTRACT

Exhaustive tests on a Westfalia model of the Fritz continuous butter-producing machine have indicated that this machine is not suited to the production of butter for the Canadian market. Considerable difficulty was encountered in producing butter to meet the legal requirement of 16%, or less, moisture. During routine commercial operation an excessive proportion of the machine's output could be expected to exceed this limit. No satisfactory method for salting the butter has been developed. Dry salt added during working of the butter did not become uniformly distributed, and caused mottling of the butter during storage.

INTRODUCTION

During recent years considerable interest has developed in procedures for the continuous production of butter. The majority of the processes being studied, or used, are based on the chilling of cream containing at least 80% butterfat, but cream containing 40 to 45% butterfat is used in a semicontinuous method developed by Senn in Switzerland, and in a continuous process developed by Fritz in Germany (8, 10). Consideration of the various factors involved led to the belief that the Fritz machine might be adapted to Canadian use. Studies designed to test this assumption were therefore undertaken at the National Research Laboratories, Ottawa, using a machine manufactured at Oelde Westfalia.

Several models of the Fritz machine, differing considerably in construction and design, have been produced and used in Germany. Several investigators have examined such machines and discussed their design and operation with the inventor (1, 2, 3, 4, 5). Some information on the machine has been published (6, 8, 9, 10) and a Roth type of Fritz machine has been studied in the United States (7). The information thus available is somewhat inconclusive, probably because of variations in the make of machines and in the creams used for churning. The machine used in the present studies was designed to produce unsalted butter containing up to 20% moisture, and it was evident that extensive studies would be required to determine how to adapt it to the production of salted

[1] *Manuscript received March 10, 1952.*
Contribution from the Division of Applied Biology, National Research Council, Ottawa, Canada. Issued as paper No. 273 of the Canadian Committee on Food Preservation and as N.R.C. No. 2765.
[2] *Present address: Defence Research Board, Ottawa.*

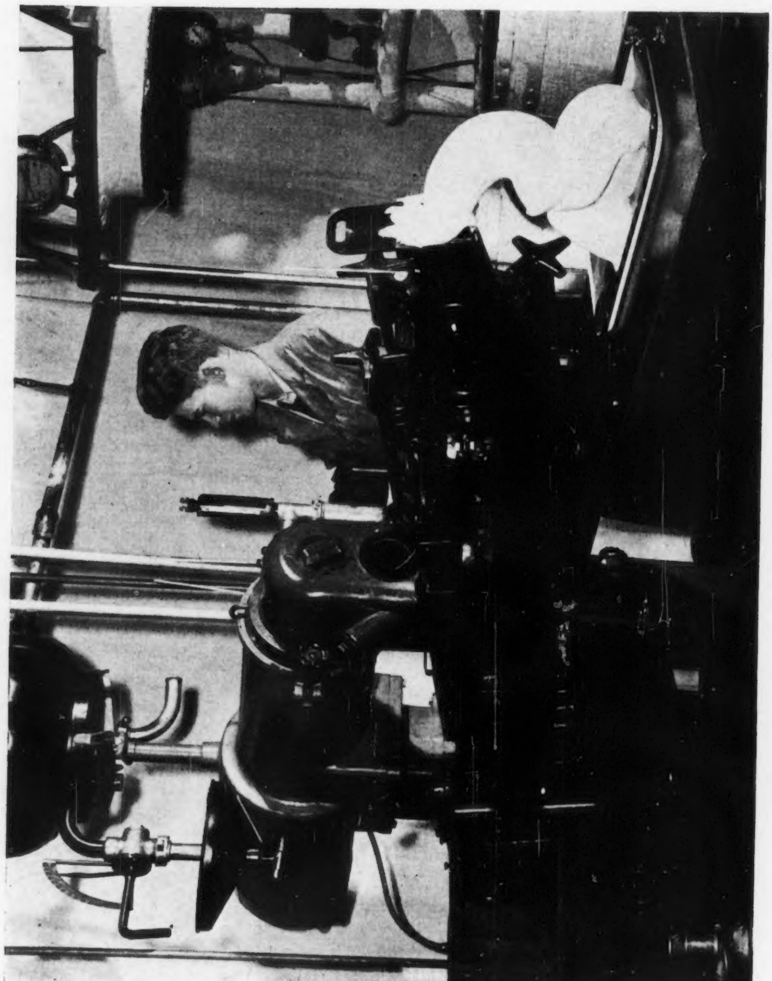


FIG. 1. Westfalia model of the Fritz continuous butter-making machine.

butter meeting the Canadian legal requirement of 16% moisture. Some 350 trials, each involving at least 45 gal. of cream were therefore made over a four year period. In this paper, a vast amount of detail on variations in cream supplies and operating techniques is omitted, and only sufficient data to illustrate the results are presented.

DESCRIPTION OF THE MACHINE

The machine is shown in operation in Fig. 1, and its construction is presented in Fig. 2, which shows a sectional view of the inversion chamber and an "exploded" view of the butter-press or separating chamber and the butter-working or kneading chamber. All surfaces in contact with cream, butter, or buttermilk are of "dural type" metal coated with a hard, durable lacquer.

Cream for churning enters the machine from an 11-gal. bowl mounted on top of the machine, and fitted with a flow control valve and a graduated quadrant. The cream enters a horizontal, cylindrical churning or inversion chamber (dimensions 9.75 in. i.d. $\times$ 21.5 in. length) surrounded by a jacket for circulating

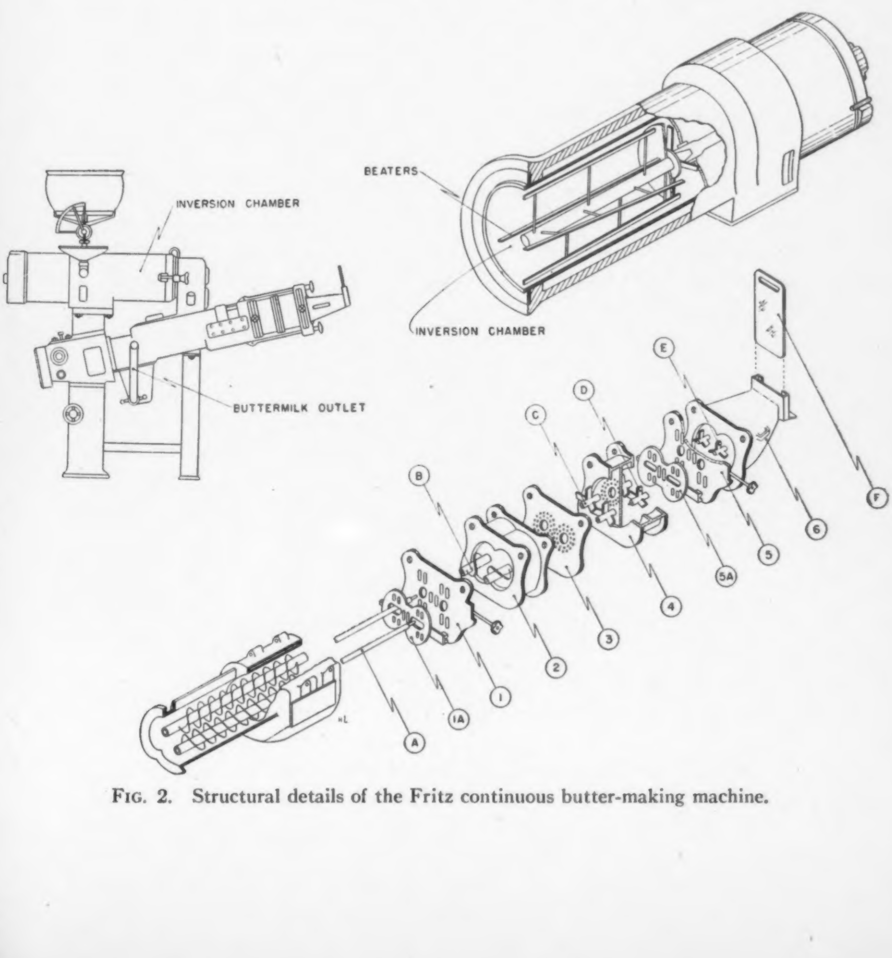


FIG. 2. Structural details of the Fritz continuous butter-making machine.

FIG. 1. Westfalia model of the Fritz continuous butter-making machine.

cooling water or brine. Within this chamber are four rotating blades, about 0.8 in. wide extending the full length of the chamber, twisted slightly along their length, and mounted with a clearance from the chamber wall of about 0.04 in. at the center and about 0.12 in. at each end. The twist of the blades is such that when rotated clockwise (viewed from the motor end) they retard the passage of cream along the chamber. Butter granules and buttermilk leaving the chamber fall on to a pair of worm-screws at the rear of the butter press (lower left hand side of Fig. 2).

The screws carry the butter up an incline of 12° to the working section (A-F), and buttermilk drains back into a catch basin and out of the machine by a gooseneck pipe. Butter is carried by the screws into a jacketed portion of the working section, and through variable control plates (1 and 1A, Fig. 2), along a short screw (B), through a plate (3) with fixed perforations, mixing paddles (C), a second plate (4), additional mixing paddles (D), a second variable plate (5 and 5A), a third set of mixing paddles (E), and finally out of the adjustable nozzle (F).

When delivered, the motor for rotating the paddles in the inversion chamber was 1460 r.p.m., 330/660v., 50 cycle, 13.5 h.p. For Canadian use, this was rewired for 550 v., 60 cycle, 15 h.p., and arranged for speeds of 1200 or 1800 r.p.m. A second motor (originally 330/660 v., 50 cycle, 3 h.p.) drove the screws at 45 or 75 r.p.m. through a gear box. After rewiring and the addition of a variable control, speeds of 20, 32, 44, 57, and 89 r.p.m. were available.

CREAM SUPPLY

In studies designed to assess the suitability of this machine for Canadian use, it was desirable to maintain conditions that conformed as closely as possible to current commercial practice in Canada. Unless otherwise stated, the prechurning treatment received by the cream was as follows:

Milk, or farm-separated cream, was passed through a De Laval "airtight" separator to give a cream of the desired butterfat content. This cream was held at about 90°F. for 10 min. and neutralized to an acidity not greater than 0.15%. It was then heated to 170-175°F., held for five minutes at this temperature, cooled to 45°F., and transformed to vats (occasionally cans) for overnight storage at 40-45°F. For tests involving cream at other temperatures, the cream was heated to the required temperature and held for three hours or longer before processing.

PRODUCTION RATE

The machine, as purchased, was said to have a production rate up to 3000 lb. per hour. Experimentally the rate of production varied from slightly less than 300 to slightly over 3000 lb. per hour, depending upon the rate of cream inflow, the fat content of the cream, and, to a lesser extent, on the rate of rotation of the inversion chamber paddles and of the screws, and on the temperature of processing.

The relation between the setting of the cream inlet valve, as indicated by the graduated quadrant, and the rate of cream flow was approximately linear for

any one batch of cream, but varied with the fat content and viscosity of different creams. Too great a flow flooded the inversion chamber and led to the extrusion of whipped cream instead of butter granules. It was therefore necessary to adjust the cream inlet valve for each lot of cream.

The production rate was, as expected, closely correlated to the fat content of the cream, the coefficient of correlation for all runs made being 0.83. The data from which this correlation was derived are presented in Fig. 3, in which each point represents one lot of cream. The data were not corrected for valve opening or flow rate.

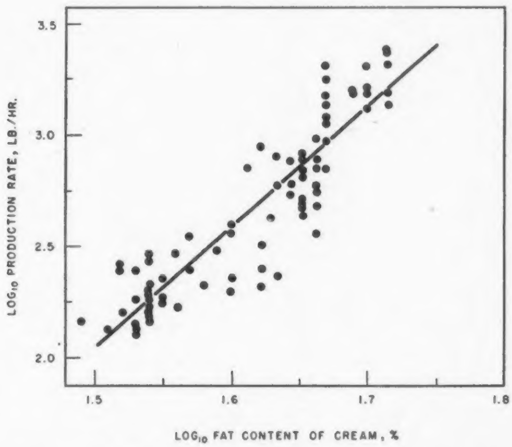


FIG. 3. Effect of fat content of the cream on the rate of butter production.

MOISTURE CONTENT OF THE BUTTER

It became obvious early in the studies on this machine that with normal operation the moisture content of the butter markedly exceeded 16%, and that reduction of this moisture level was a major problem to be overcome in adapting the machine for Canadian use. Extensive studies were therefore made to determine the effect of several variables on the moisture content of the butter.

Various mechanical alterations were made without any apparent effect on the moisture content. These included adjustment of the clearance of the paddles from the inversion chamber wall, removal of two of the four paddles, reversing the direction and varying the speed of rotation of the paddles, adjustment of the position of the inversion chamber outlet with respect to the screws, adjustment of the slope of the butter screws (varied by tilting the whole machine), and 16 minor alterations in the parts of the working section, including the addition of extra plates. Alteration of the clearance of the paddles to 0.04 in. throughout their entire length had an undesirable effect in that it lowered the production rate and increased the loss of butterfat to the butter milk (Table I). Reversing the direction of the paddles also had an undesirable effect (Table II) as it reduced

TABLE I

EFFECT OF SPACING OF CHURNING PADDLES ON PRODUCTION OF BUTTER
(Averages for six trials)

Fat content of cream, %	Paddles of 0.04 in. from walls of chamber		Paddles at original setting	
	Production rate, lb./hr.	Butterfat in buttermilk, %	Production rate, lb./hr.	Butterfat in buttermilk, %
42	255	1.0	—	—
45	380	1.2	670	0.4
48	582	1.4	1370	0.8
52	—	—	1835	1.2

TABLE II

EFFECT OF DIRECTION AND RATE OF ROTATION OF PADDLES IN THE INVERSION CHAMBER ON PRODUCTION OF BUTTER

(Averages for at least two trials)

Factor varied	Production rate, lb./hr.	Moisture content, %	Butterfat in buttermilk, %
Paddle direction			
Clockwise	680	26.5	0.8
Counterclockwise	140	32.8	3.5
Paddle speed			
1800 r.p.m.	690	22.9	0.9
1200 r.p.m.	320	24.8	1.5

the efficiency of conversion and markedly lowered the production rate. Decreasing the speed of the paddles also lowered the production rate (Table II).

Slow screw speeds gave butter of a lower moisture content than did high speeds, presumably because of the longer period thus allowed for the drainage of buttermilk from the butter granules. However, the minimum rate of screw rotation was fixed by the necessity of preventing an overaccumulation of butter granules in the drainage section, and low screw speeds could only be combined with the use of low fat content creams or low inflow rates. This method of moisture control thus necessitated low production rates.

The fat content of the cream, acidity of the cream after neutralization, temperature of pasteurization, and length of holding time between pasteurization and processing were without effect on the moisture content of the butter or on the loss of butterfat. The temperature of the cream and butter during processing could be controlled, within limits, by varying the temperature of the inflowing cream and the temperature of the cooling fluid in the jackets on the inversion chamber and butter-working sections. Circulation of water at about 40°F. through the jacket of the inversion chamber did not have sufficient cooling effect to offset the heat input of the paddles, and an average temperature rise of 7°F. was observed during the fraction of a second required for the passage

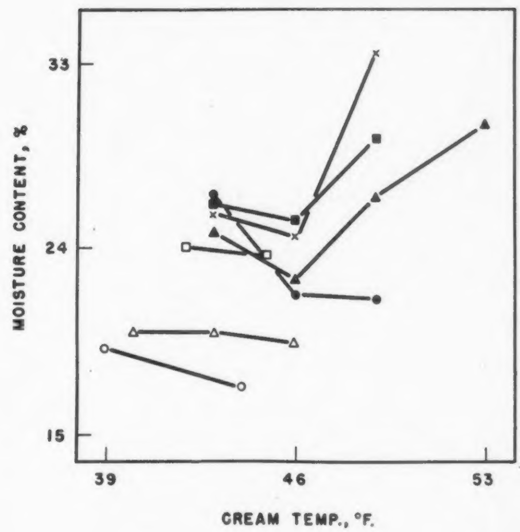


FIG. 4. Effect of cream temperature on the moisture content of the butter produced from winter cream. Each line represents a series of trials on a single batch of cream.

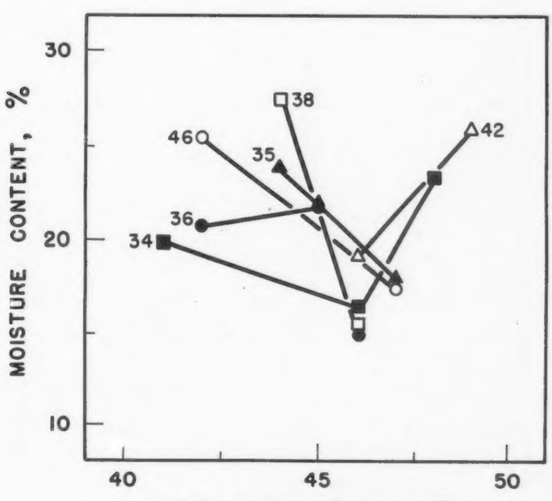


FIG. 5. Effect of cream temperature on the moisture content of butter produced from summer creams. The numbers indicate the fat content of the cream, but each point represents a different batch of cream.

of cream through this chamber. Some heating also occurred in the butter-working section, the amount depending in part upon the rate of movement of the butter past the cooling jacket, i.e., upon the rate of production.

Seven lots of cream obtained during the winter were subdivided and the sublots churned at different temperatures to determine the effect of cream temperature on moisture content of the butter. The data obtained (Fig. 4) reflect the variability encountered in different lots of cream, and suggest that, for each lot, butter of the lowest moisture content was produced from cream at 46°F. The effect of cream temperature on the processing of summer creams was not studied independently of other factors, but the available data are presented in Fig. 5. Each point on this figure represents data from a single lot of cream;

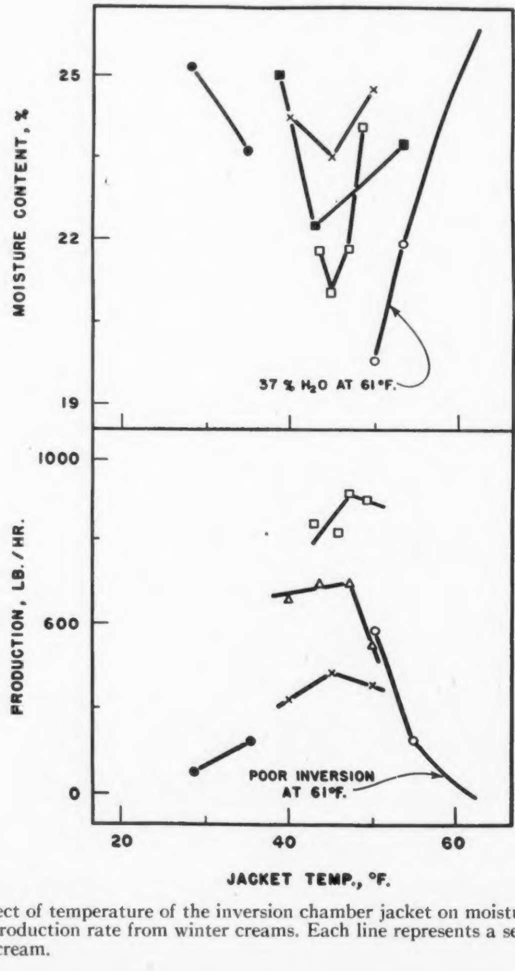


FIG. 6. Effect of temperature of the inversion chamber jacket on moisture content of the butter and on production rate from winter creams. Each line represents a series of trials on a single batch of cream.

creams of equal fat content have been joined by lines. There was no detectable relation between butterfat content of the cream and moisture content of the butter, but again there appeared to be a minimum moisture level with creams processed at a temperature close to 46°F.

Data on the effect of the temperature of the inversion chamber jacket on moisture content and production rate are presented in Figs. 6 and 7. Fig. 6 refers to creams processed during the winter months and Fig. 7 to summer creams, each line representing a series of trials on sublots of a single batch of cream. For processing winter creams the optimum jacket temperature for production of low-moisture butter appeared to be about 45°F., for summer creams it appeared to be at or below 40°F. Limited refrigeration capacity prevented

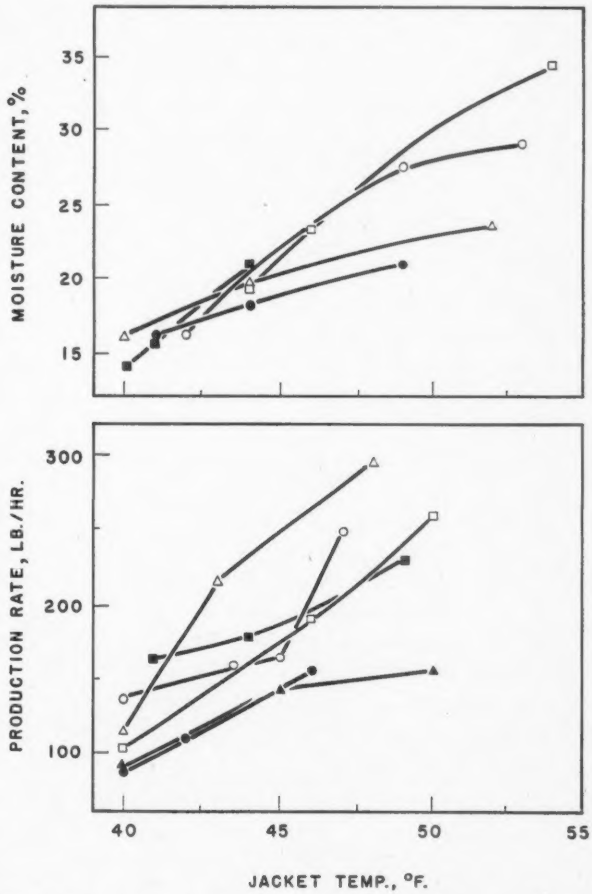


FIG. 7. Effect of temperature of the inversion chamber jacket on moisture content of the butter and on production rate from summer creams. Each line represents a series of trials on a single batch of cream.

study of a range of temperatures below 40°F. but, when brine at 26°F. was circulated through the jacket, an increase in the moisture content of the butter over that found at 40°F. occurred. For the production of low moisture content butter from summer creams there may, therefore, be an optimum jacket temperature somewhere between 26° and 40°F.

Over the relatively narrow range of temperature control obtainable by direct means (i.e., control of cream and inversion chamber jacket temperatures) there was a significant direct correlation between the temperature of the butter granules and buttermilk falling from the inversion chamber and the moisture content of the butter. The heat input of the inversion chamber paddles made it difficult to obtain butter granules at less than 45°F. To extend the temperature range, on a purely experimental basis, attempts were made to obtain lower temperatures by spraying cold water, dry ice, or liquid air onto the granules and buttermilk as they fell from the inversion chamber. Cold water did not cool the granules sufficiently to have any effect. Liquid-air or dry-ice sprays effected some reduction in moisture content of the butter when the screws were operated at 32 r.p.m., and a dry-ice spray was particularly effective when the screws were operated at 20 r.p.m. However, these extremely cold sprays froze buttermilk to the granules, and thus nullified some of the beneficial effects.

Water at an average temperature of about 42°F. and brine at 12°F. were available for cooling the jacket on the butter working section. At very low production rates, which allowed more time for heat exchange between butter and cooling fluid than did high production rates, cooling with brine at 12°F. maintained the butter temperature a few degrees below that obtained when cooling with water at 42°F. Cooling with brine under these conditions also resulted in a lower moisture content in the butter. At high production rates the cooling effect of the fluid in this jacket would be nullified by the heat input of the screws.

TABLE III

EFFECT OF TEMPERATURE OF COOLING FLUID FOR THE BUTTER-WORKING SECTION ON PRODUCTION OF BUTTER

(Production rate, 250 lb./hr. or less; screw speed, 20 r.p.m. Each horizontal line of figures represents tests on a single lot of cream, but the columns of figures represent different cream lots which varied in fat content, source, and age)

Temperature of butter granules, °F.	Temperature of outgoing butter, °F.		Moisture content of butter, %	
	Water cooling (42°F.)	Brine cooling (12°F.)	Water cooling (42°F.)	Brine cooling (12°F.)
52	57	48	24.6	14.0
53	58	52	16.1	14.8
54	58	53	27.4	18.5
54	59	57	23.4	18.8
55	57	52	24.6	17.4
56	58	54	18.1	11.4
58	59	56	22.8	19.4
Av. 54.5	58.0	53.1	22.4	16.3

SALTING THE BUTTER

Since the Canadian demand for unsalted butter is limited, various means of introducing salt into the machine were tested. Addition of salt as a concentrated brine was not practical because of the large amount of water introduced. Dry salt was successfully forced into the lower portion of the working section (near the second plate) with a variable speed worm injector. Satisfactory control of the amount of salt introduced was obtained, but the salt crystals failed to dissolve and become uniformly distributed in the aqueous phase of the butter. This led to mottling of the butter during storage. The use of damp salt effected no improvement. Introduction of salt at earlier stages was considered, but such procedures are wasteful of salt and spoil the buttermilk for feed purposes.

QUALITY OF THE BUTTER

Attempts were made to compare various chemical and physical aspects of Fritz and churn butters, but failure to obtain the two butters at the same moisture level rendered the data inconclusive, except those on curd content. No means are available for washing butter during its production in the Fritz machine, and the curd content is therefore higher than that of normally washed churn butter. For the three most comparable samples obtained, Fritz butter contained 1.2, 1.4, and 1.7% curd, churn butter 0.5, 0.8, and 0.7% respectively.

CONCLUSIONS

In general, these studies have indicated that the Fritz machine is not suited to the Canadian butter-making industry. Firstly, it appears to be impossible to produce a salted butter without drastic changes in design, and there is little or no demand for unsalted butter on the Canadian market. Secondly, control of the moisture content of the butter at or below the legal requirement of 16% is extremely difficult; in fact our experience suggests that with some lots of cream it is impossible to reduce the moisture content to this level.

The machine does offer a rapid and convenient means of concentrating butterfat from 35 to 45% creams, and it may have a use in other phases of the dairy industry, e.g., the preparation of fat for use in ice cream mixes, etc. For such purposes close control of the moisture level would not be essential, and high rates of production would be possible.

ACKNOWLEDGMENTS

The authors wish to express their sincere thanks to Dr. J. W. Hopkins for statistical treatment of some of the data, and to Messrs J. Marier and G. Belanger for assistance with the operation of the machine.

REFERENCES

1. B.I.O.S. Rept. Item Nos. 22 and 31, Final Rept. No. 85.
2. B.I.O.S. Rept. Item No. 22, Final Rept. No. 275.
3. B.I.O.S. Rept. Item No. 22, Final Rept. No. 770.
4. C.I.O.S. Rept. Item No. 22, File No. XXXII-49.
5. C.I.O.S. Rept. Item No. 22, File No. XXXIII-22.
6. Cook, W. H. Food in Canada, 6: 24-28. 1946.
7. Fifer, F. Am. Butter Rev. 9: 25-26. 1947.
8. Fritz, W. Chem.-Ztg. 67: 115-117. 1943.
9. Wiechers, S. G. and De Goede, B. Continuous butter making. North-Holland Publishing Co., Amsterdam. 1950.
10. Wilsmann, W. and Feltens, E. Die Milchwissenschaft, 2: 307-309. 1947.

THE PREPARATION OF ANHYDROUS ALUMINUM CHLORIDE[1]

BY W. DAVID ENGLISH

ABSTRACT

An investigation has confirmed that a mixture of chlorine and hydrogen chloride is much more efficient for the production of anhydrous aluminum chloride from aluminiferous materials than either gas alone. The temperature of the reaction can be decreased to as low as 500° C. while maintaining attractive conversion rates.

In the preparation of anhydrous aluminum chloride from nonmetallic sources, the work of Spitzin and Gwosdewa (1) seems to have been overlooked, possibly because of an error in Chemical Abstracts (2). For instance, Thomas (3) makes three references to their paper in his summary of methods for the preparation of anhydrous aluminum chloride, yet does not mention their use of mixed gases. These authors report that a mixture of hydrogen chloride and chlorine is more efficient for the production of aluminum chloride from clay than either gas alone. In the abstract the opposite is stated as their conclusion.

In these laboratories it was found that when alumina, either pure or that obtained by calcining aluminum chloride hydrate, was mixed with carbon and chlorinated, the conversion per hour (per cent of theoretical yield obtained in one hour) was greater for a mixture of chlorine and hydrogen chloride than for either gas alone. With such mixtures appreciable reaction took place at 500°C., and yields were excellent in the range 500-600°C. Chlorine alone requires 800-900°C., hydrogen chloride alone requires 1000°C.

The most efficient mixture of gases was two parts chlorine, one part hydrogen chloride and one part nitrogen by volume. Other mixtures were not as efficient, but any mixture of chlorine and hydrogen chloride with or without inert gases was much better than either chlorine or hydrogen chloride alone or with diluents.

The presence of oxygen in the chlorine–hydrogen chloride mixture decreased the conversion somewhat, but burned carbon, thus decreasing the amount of heating necessary. Thus Deacon gas could be used after drying.

A summary of the experimental results is given in Table I.

EXPERIMENTAL

The apparatus consisted of a satin-quartz tube heated with an electric furnace (Fig. 1). To this was connected (S.T. joints) a large pyrex tube which acted as an air condenser. The connection was kept at 300°C. to prevent condensation of aluminum chloride. The reaction tube and condenser were used in a horizontal position. Temperatures were measured by thermocouple, gas volumes by flowmeters.

One experiment is described to show the method. A mixture of 40 gm. of reagent aluminum chloride hexahydrate with 7 gm. of activated charcoal was

[1] *Manuscript received April 29, 1952.*
Contribution from Defence Research Chemical Laboratories, Ottawa 2, Ontario. Issued as D.R.C.L. Report No. 75A.

TABLE I

VARIATION IN YIELD OF $AlCl_3$ CAUSED BY CHANGED REACTION CONDITIONS

Ratio of solids		Ratio of gases				Temperature, °C.	Conversion, % per hr.
Al_2O_3	C	HCl	Cl_2	N_2	CO_2		
1*	3	5	–	2	–	1000	3
1*	9	–	1	1	–	1000	19
1*	2.5	1	2	1	–	800	100% in < 2 hr.
1*	7	1	2	1	–	600	45
1	3	1	2	1	–	650	56
1*	5	1	2	1	–	500	10
1*	3	1	1	9**(air)	–	600	26
1	1.2	2	1	1	–	500	11
1	1.2	2	1	1	–	600	27
1	1.2	1	1	–	–	500	15
1	1.2	1	1	–	–	600	38
1	1.2	1	1	4	–	500	4
1	1.2	1	1	4	–	600	34
1	1.2	1	2	–	1	600	31

**Al_2O_3* from calcination of $AlCl_3.6H_2O$.*
***This was a synthetic mixture made up to approximate the chlorine-containing exit gas from a Deacon reactor.*

placed in the reactor. The furnace temperature was set at 1000°C. and nitrogen was passed through until no more water came off. The temperature was lowered to 800°C. and a mixture of chlorine, hydrogen chloride, and nitrogen (2:1:1 v/v) was passed through at a total rate of 400 ml. per min. Product condensed in the Pyrex air condenser. The condenser was weighed after four and one-half hours. The gain in weight was 22 gm. (100% of the theoretical). Analysis. Found: Al, 21.2%; Cl, 79.3%. Calculated for $AlCl_3$: Al, 20.2%; Cl, 79.8%.

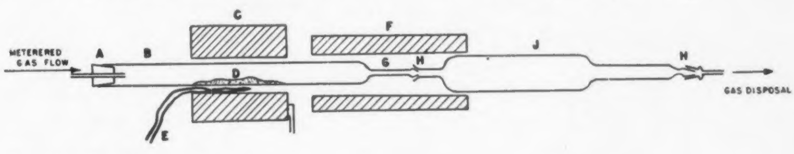


FIG. 1. Experimental reactor.

A. Rubber stopper
B. Fused satin quartz reactor
C. High Temperature electric furnace
D. $AlCl_3.6H_2O + C$
E. Thermocouple
F. Low Temperature electric furnace (300°C.)
G. Quartz-to-pyrex seal
H. 19/38 S.T. pyrex joint
J. Large condenser

CONCLUSION

Mixtures of chlorine and hydrogen chloride, with or without inert diluents are more efficient in the chlorination of alumina mixed with carbon than either gas alone. The optimum gas mixture was two parts chlorine, one part hydrogen chloride, and one part nitrogen.

REFERENCES

1. SPITZIN, V. I. and GWOSDEWA, O. M. Z. anorg. u. allgem. Chem. 196: 289-311. 1931.
2. STOERTZ, H. Chem. Abstracts, 25. 2381. 1931.
3. THOMAS, C. A. Anhydrous aluminum chloride in organic chemistry. Chap. 20. Reinhold Publishing Corporation, New York. 1941. pp. 849, 852, and 854.

AN EXPERIMENTAL RESIDENTIAL HEAT PUMP[1]

By F. C. Hooper[2]

ABSTRACT

A research project has been undertaken by the University of Toronto to investigate the applicability of the heat pump system to residential heating in Ontario. An experimental installation consisting of a ground-source heat pump, supplemented by resistance heaters, was made in an occupied residence.

Data obtained from the 1949–50 heating season on the characteristics of the electric load, on the heating performance, and on the operation of the ground coil have been analyzed. The performance of this heat pump system has been sufficiently encouraging to warrant further investigation, and the project has been continued through 1951 and 1952.

INTRODUCTION

In Ontario, as elsewhere, there is a growing interest in the potential usefulness of the electrically driven heat pump as a residential heating and air-conditioning device. In view of this interest, the need for reliable data on the applicability of the heat pump system under Canadian climatic and economic conditions is apparent. An investigation was started in 1949 by the University of Toronto in order to provide significant and applicable data.

Specific information is being sought on the suitability of the available heat sources, the characteristics of the load which would be imposed on the electrical utility, and the compatability of the heat pump with domestic requirements.

In the initial approach to these questions it was decided to install and to operate under careful observation, a heat pump system in an occupied residence. The objective was to make a practical working installation which would be indicative of future applications and would provide significant experimental data and confirmation of estimated factors.

The 1949-50 heating season results are reported here. The experiment has been continued throughout 1951 and 1952, and a further report at a later date will offer the additional data which have been obtained.

SELECTION OF A REPRESENTATIVE INSTALLATION

The type of heat source is of controlling importance and was necessarily the first decision to be made. Because of the temperatures prevailing in Canada throughout the greater part of the heating season, the coefficient of performance would be unattractively low if the outdoor air were used as the source. Moreover, serious coil icing problems would be encountered. Therefore air was considered to be unsuitable.

Ground water, although possessing several advantages, is not generally available for this use. For this reason, and in consideration of well-digging and

[1] *Manuscript received January 11, 1952.*
Contribution from the Department of Mechanical Engineering, University of Toronto, Toronto, Canada.
[2] *Lecturer in Mechanical Engineering.*

pumping costs, and of ground water depletion and freezing difficulties, this source was rejected.

Combined heat sources, such as air coils with auxiliary ground coils, require complicated controls and high initial expenditure, and were rejected without detailed analysis.

The ground coil, although presenting local installation and design problems, provides a stable heat source at a reasonable temperature level and one not hampered by icing conditions. The choice therefore devolved upon the ground as a heat source. Since vertical coils are unworkable, it was decided to utilize a horizontal ground coil.

The heat transfer fluid to carry the heat from the ground coil must be either the heat pump refrigerant or a secondary circulating liquid. Although the direct expansion system, utilizing the refrigerant in the ground coil, eliminates one heat transfer operation, it has several serious disadvantages. These include installation difficulties and risks of leakage, vapor locking, and clogging. The use of a low-cost liquid in the coil minimizes these difficulties although this method requires an additional auxiliary circulating pump and heat exchanger. Accordingly a secondary liquid system was chosen because of its positive operating characteristics, and also because it permits simple and accurate measurement of the heat quantities.

Direct forced air was selected as the house-heating medium mainly because this system is readily adapted to summer cooling. Panel heating, although attractive from the temperature and coefficient of performance consideration, cannot be adapted to summer use because of condensation problems.

The practical aspects of the experiment dictated the use of a package type heat pump. Only one type of packaged unit intended for such a ground-to-air installation was being manufactured and therefore this type of unit was used in the experimental installation.

Economically, the most favorable heat pump heating system is sized to carry only a portion of the maximum instantaneous house heating load, but at the same time it should provide a large proportion of the total annual heat requirement. The instantaneous deficiencies in heating capacity would be made up by some supplementary means. This additional heat is very conveniently supplied by resistance-type heaters. Under local conditions a unit which meets one-half of the instantaneous maximum heating demand is adequate for complete summer cooling. Hence an approximately equal division of heating capacity between a packaged heat pump and resistance heaters would be satisfactory.

A new house of average size, construction, and occupancy was chosen for the experimental installation. A lot of adequate size was available at this site.

DESCRIPTION OF INSTALLATION

The experimental installation was completed in October 1949. The five room, single storey house chosen was of masonry construction, with insulated walls and ceiling. The heat pump was conveniently located in a corner of the basement.

The packaged unit consisted of a double-twin Freon 12 compressor, belt driven by a 3 h.p., 25 cycle, 230 v., repulsion-induction motor. The layout of the unit with its auxiliaries is shown in the flow diagram (Fig. 2). An ethyl alcohol and water antifreeze mixture was circulated in the ground coil system. Three 2 kw. supplementary resistance heaters were located in the delivery air duct downstream from the heat pump condenser coil. A conventional forced warm air ducting system was used to distribute and return the air.

Soft drawn $\frac{3}{4}$-in. copper tubing was used for the ground coil system. Three circuits, each with an effective length of approximately 300 ft., were laid in the grounds of the residence. They were placed at a depth of 5 ft. and at a horizontal spacing of 6 ft. A trenching machine, supplemented by hand labor, proved to be effective in the coil-laying operation. The layout of the coils is shown in Fig. 1.

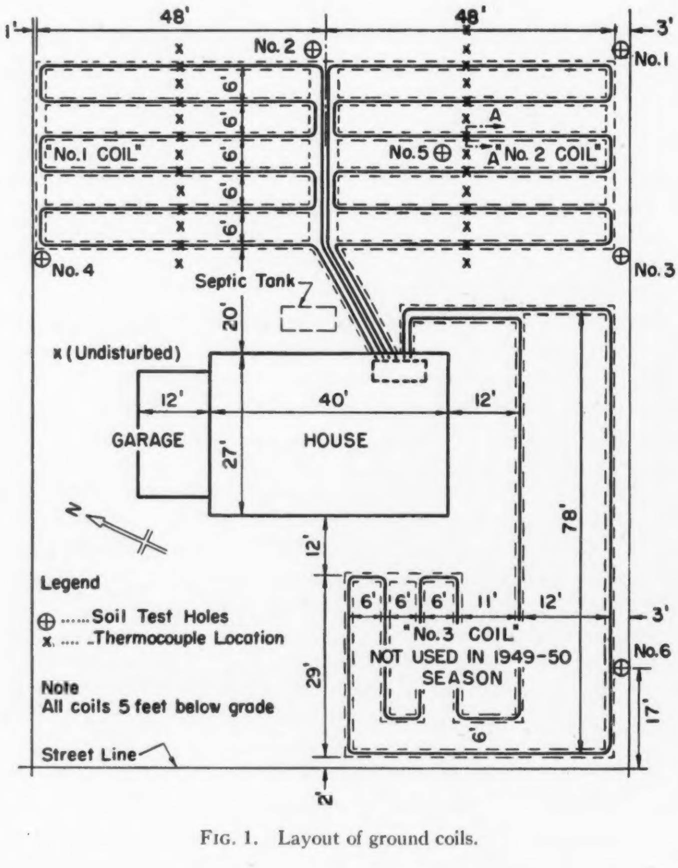


FIG. 1. Layout of ground coils.

A four step, modulating, thermostatic control actuated by the air temperature of the house was arranged to bring the heat pump and the three resistance heaters into operation. The control steps were at approximately one degree Fahrenheit intervals, with the heat pump at the first operating point, and one 2 kw. heater at each succeeding point. Under this arrangement the heat pump took the base heat load, supplemented only when necessary by the heaters. The resistance heaters were operated on off-peak power only, under time clock control. Safety controls were fitted to the compressor, the motors, and the electric heaters.

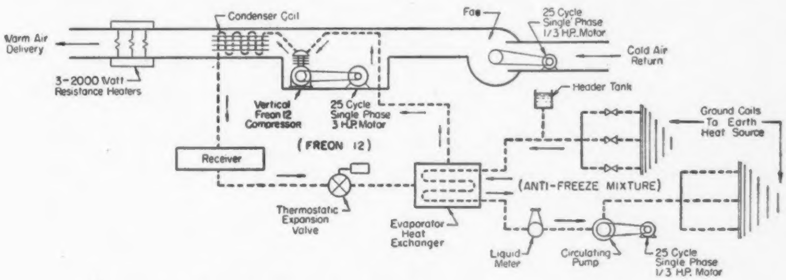


FIG. 2. Flow diagram of heat pump system.

Significant electrical and thermal quantities were measured. The instrumentation provided is tabulated in Table I. Additionally, check readings were made periodically with laboratory instruments. The instrument and control panel is shown in Fig. 3.

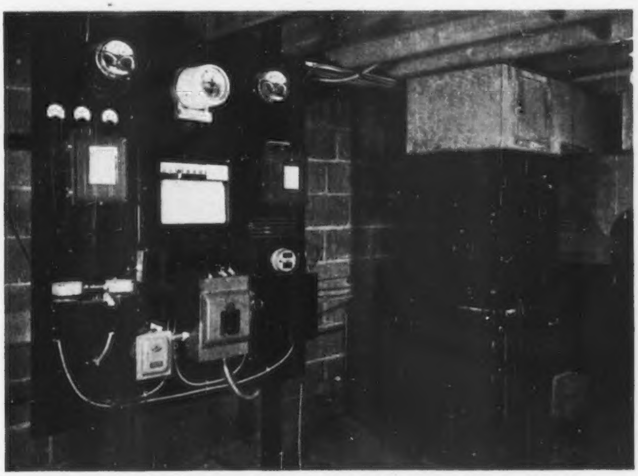


FIG. 3. Instrument and control panel with the heat pump unit.

TABLE I

INSTRUMENTATION

Quantity measured	Instrument	Number of instruments	Location
Electric energy consumption	Integrating watt hour meter	3	Heat pump motor; heat pump auxiliaries; resistance heaters
Maximum power demand	Indicating demand meter	1	Total power supply
Instantaneous load current	Recording ammeter	1	Total power supply
Instantaneous line voltage	Recording voltmeter	1	Supply line
Operating time	Totalizing clock	4	Heat pump and each of three heaters
Ground temperatures	Thermocouples and potentiometer	–	About ground coils
Antifreeze temperature differences	Thermopile and recording potentiometer	1	Across ground-coil supply and return pipes
Air temperatures	Recording potentiometer	1	Outdoor air; warm air supply; room air
Antifreeze flow	Integrating liquid meter	1	Ground-coil supply pipe
Antifreeze specific gravity	Hydrometer	1	Header tank
Refrigerant pressures	Bourdon gauges	2	Compressor suction and delivery

GROUND COIL DESIGN AND PERFORMANCE

Because the experimental residence offers more surrounding ground than is normally available, two of the coils, Nos. 1 and 2 on the plan, were laid in a plot 30 by 100 ft., to correspond to the area available in an average lot. These two coils only were operated in the 1949-50 heating season, the third coil being held in reserve for future experiments. The two circuits used have an effective length of 612 ft.

The copper tubing was chosen for reasons of durability and ease of handling. The diameter was based upon the economic balance between initial tubing cost and circulating pump power requirements. The decrease in the over-all thermal resistance between the circulated fluid and the bulk of the soil with increasing tube diameter is small and was not a factor in this choice.

The number of parallel circuits employed to give the necessary coil length was a compromise between low pumping power requirements and coil fluid temperature rises, and the experimental requisites. The coil lengths per circuit are somewhat greater than would normally be chosen.

The 5 ft. depth was dictated by the limitations of the trenching machine employed, and the 6 ft. spacing by the assumed typically available land area. For best coil performance with due allowance for annual recovery, a depth of between 6 and 8 ft. is indicated, although increased spacings up to 15 ft. would be desirable if ground areas were available. However, the actual values used are close to the economic balance point for average conditions.

To avoid the possibility of damage to the house footings through frost action, and to facilitate machine trenching, the coils were kept at least 12 ft. from the foundation line. The connections from the basement to the ground coil were made with insulated pipes, laid in the normal surface frost layer. Adequate coil length limits the diameter of the frozen core about the coil, and reduces the necessity for these precautions.

Considerable attention was given to the significant soil properties. The soil at the site is a very fine sand. It is classified as permeable and offers very limited resistance to the flow of water. Its sieve characteristics are shown in Table II.

TABLE II
MECHANICAL ANALYSIS OF COIL BED SOIL*

Sieve Number	Per cent passed
20	100
40	99.9
60	99.7
140	83.6
200	23.5

**Description of soil: very fine sand.*

The moisture content and the thermal conductivity at various depths were taken periodically in test holes at several points on the property. Moisture was measured by the conventional sampling technique. Thermal conductivity was measured by the newly developed thermal conductivity probe technique (2) which permits very rapid measurement of this property of the soil *in situ*.

Fig. 4 shows typical observations at two test holes in the coil area. The peculiar inversion of the thermal conductivity observed at the 5 ft. depth is not understood, but check tests have not revealed any instrumentation errors. The sharp increase of moisture, and consequently of thermal conductivity, with increased depth is a most important factor in the ground coil performance. The advantage of a moist site is obvious.

It is generally recognized that moisture migrates from the warmer to the cooler position. This effect assists the heat transmission toward the coil on the heating cycle both by increasing the conductivity and by contributing the convected heat of the moisture. Under the summer cooling cycle conditions a decreasing conductivity would be expected because of soil-drying in the vicinity of the coil. In Canada, the summer cooling load is so small that this reversal is of little consequence. Where coils are located below the water table this effect would not be significant.

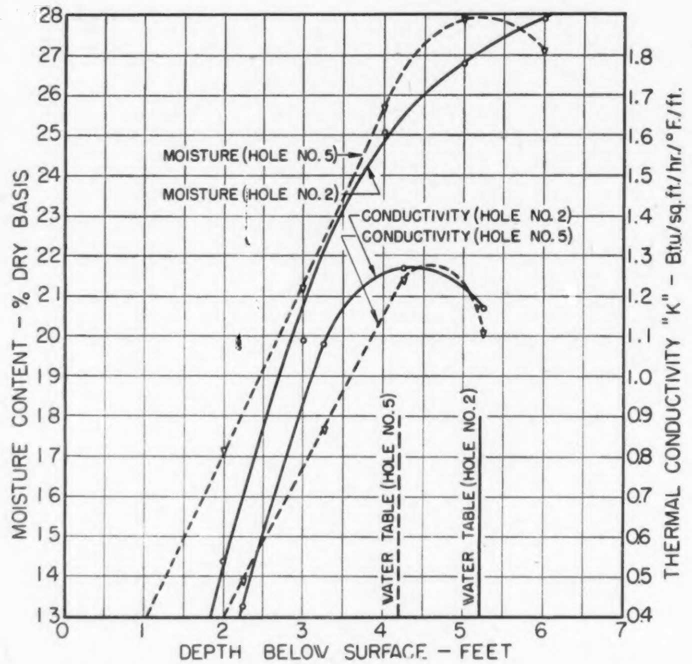


Fig. 4. Typical soil moisture and thermal conductivity observations. Hole No. 2. Outside coil area. Hole No. 5. Center of coil area (see Fig. No. 1).

Ground temperatures were measured by copper–constantan thermocouples set in crisscross patterns about the coils. The general locations of these thermocouples are shown in Fig. 1. Figs. *5a*, *5b*, and *5c* show the record of ground temperatures at the section marked A-A, over the test heating season.

To interpret the ground coil data it is necessary to understand that the ground is influenced only by the average rate of heat withdrawal. Thus, although a heat pump may be capable of withdrawing 50 units of heat per unit length of coil at the particular temperature of the coil, if it operates only 50% of a day, the average rate of heat withdrawal will be 25 units per unit length. Also, the heat withdrawal capacity of a heat pump and the coefficient of performance depend upon the source temperature. The capacity falls as the source temperature is reduced. When a heat pump is designed to carry the base heat load but not to meet the maximum heat demand it will tend to operate nearly full time in the cold months. During this part of the season the instantaneous heat pump capacity or withdrawal rate will tend to coincide with the average withdrawal rate. Curves *B* and *C* of Fig. 6 show the actual values of these quantities for the test installation, and demonstrate this behavior.

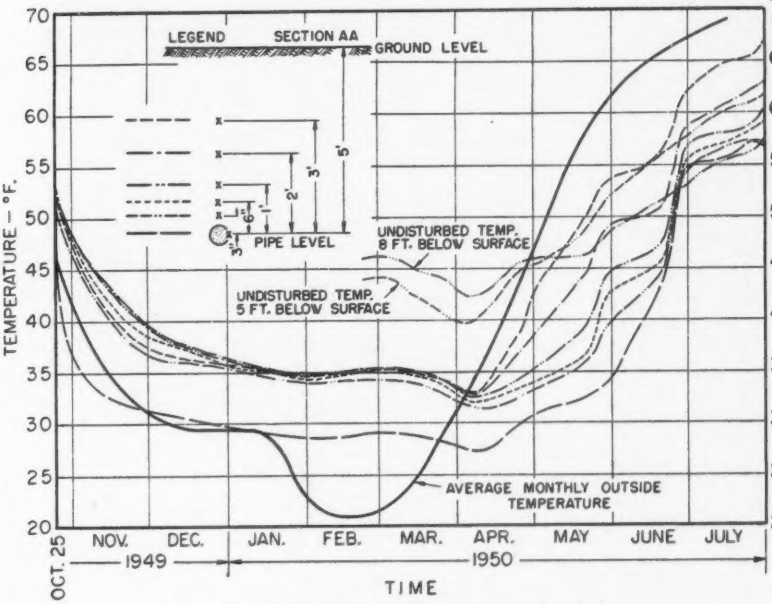


FIG. 5*a*. Ground temperatures at coil section A-A.

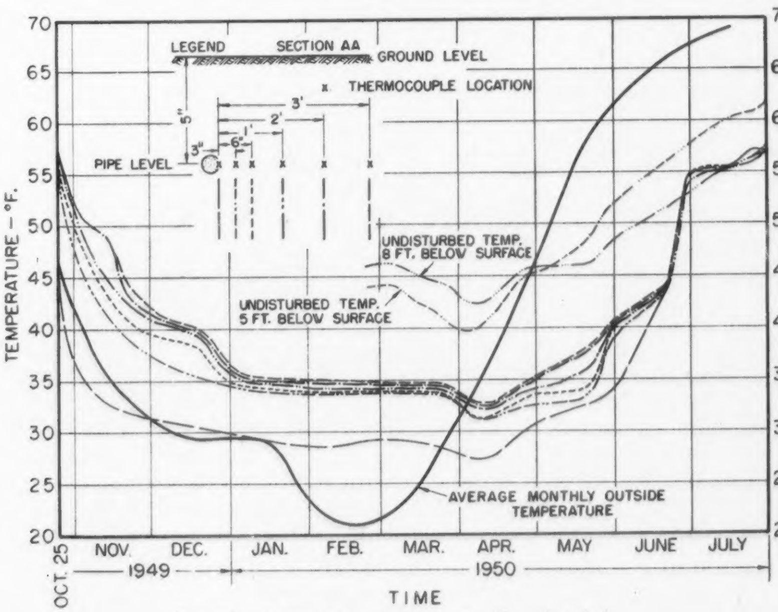


FIG. 5*b*. Ground temperatures at coil section A-A.

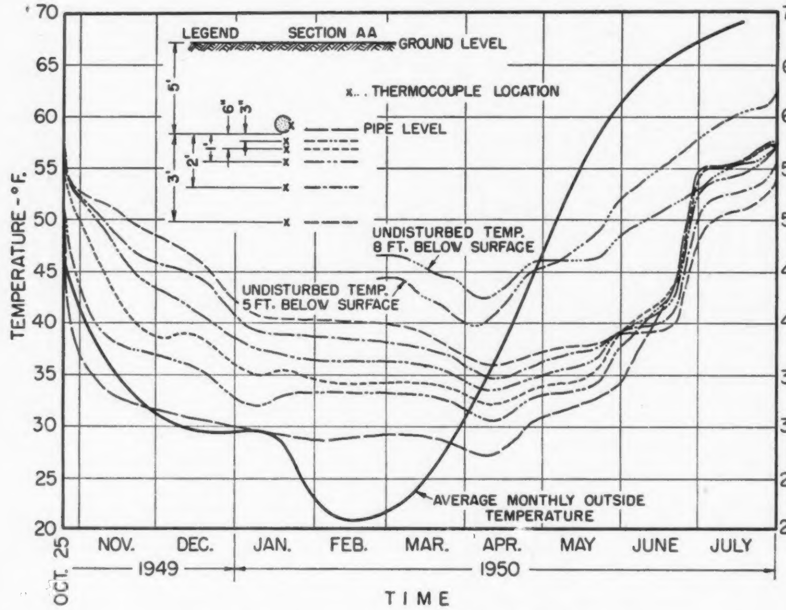


FIG. 5c. Ground temperatures at coil section A-A.

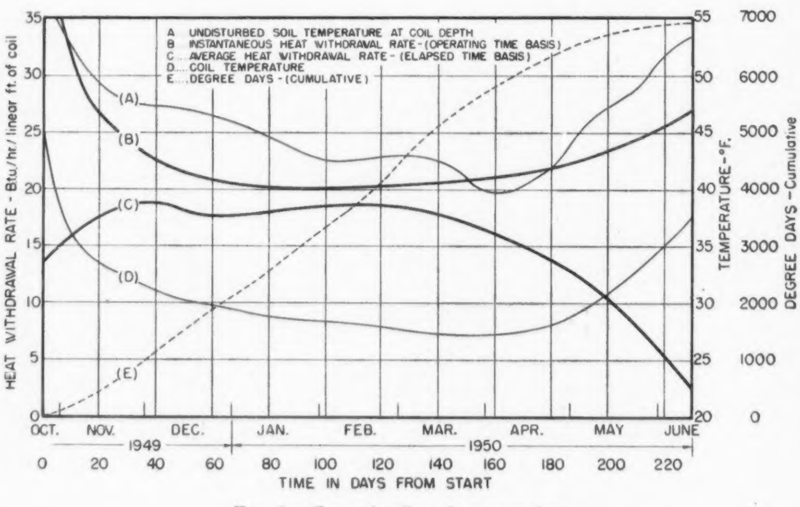


FIG. 6. Ground coil performance data.

The reduction of heat withdrawal rate with lower source temperatures tends to bring about a nearly steady state heat flow condition about the ground coils more rapidly than would otherwise occur, and this steady state represents the limiting rate of heat withdrawal for the heat pump installation. Examination of Fig. 6 will reveal this stable period from January to March, and show the limiting rate of heat withdrawal for this installation to be approximately 19 B.t.u. per hour per linear foot of coil.

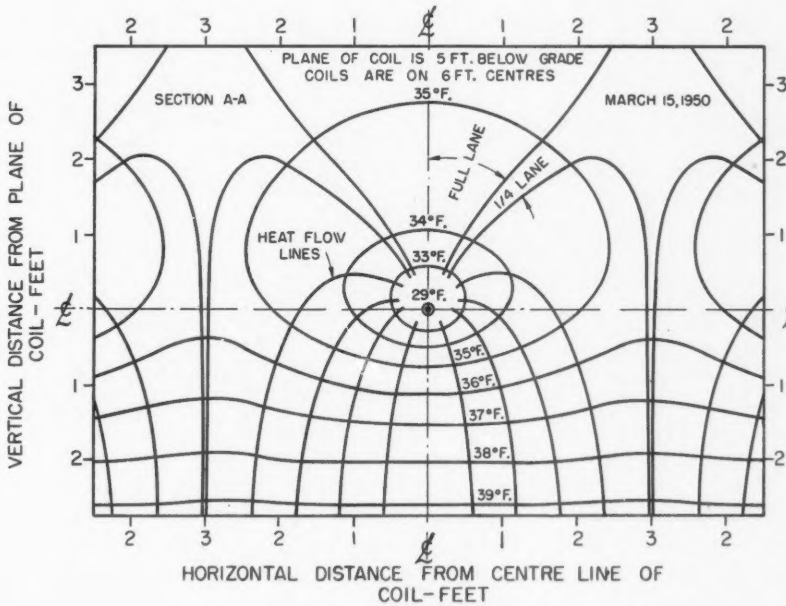


FIG. 7. Heat flow pattern about the ground coil.

The ground temperatures shown in Figs. 5*a*, 5*b*, and 5*c* also stabilize in this period, when the thermal conductivity of the soil, instead of its thermal capacity or diffusivity, controls the heat flow rate. From these ground temperature records the isothermal patterns for Section A-A of the coil can be plotted for any time during the season. In Fig. 7 this has been done for March 15, a day near the end of the stable period.

By taking advantage of the nearly steady state at this time, a modification of the method of curvilinear squares can be used to divide the field into a number of heat flow lanes, along each of which an equal quantity of heat is flowing to the coil. It is seen from the figure that 12.5 such lanes were obtained in this case, 10 of which have their origin below the coil. That is, 80% of the heat is being drawn from below the coil.

From the figures it can be seen that the average heat withdrawal rate for this day is 17.7 B.t.u. per hour per foot of coil, and that the temperature gradient is 0.55 ft. per degree at the 39°F. isotherm where the isothermal surface is nearly planar. By recalling that the tube pitch is 6 ft., the apparent thermal conductivity is calculated as:

$$k = 0.80 \times 17.7 \times 1/6 \times .55 = 1.3 \text{ B.t.u. ft.}^{-1}\text{. hr.}^{-1}\text{. °F.}^{-1}$$

Fig. 4 (hole No. 2) gives the measured thermal conductivity at a depth of 5 ft. at the same location, and at approximately the same date, as 1.23. Since the thermal conductivity normally increases somewhat with depth, this is considered to be excellent agreement. Because of this agreement, and because the nearly steady state coincides with the limiting rate of heat withdrawal which is the design basis for a coil, one is encouraged to believe that ground coils can be designed on the steady state assumption, utilizing a thermal conductivity measured by probe at the site.

A proportion of upward heat flow of 80% is not general for all cases. It would be expected to vary with depth and temperature difference between the coil and the surface. Rough calculations of the possibilities indicate that under Canadian conditions where frost sets the upper crust temperature, this proportion probably does not vary by more than 10%. The time to reach equilibrium would also vary with soil properties, and probably with coil pitch and depth.

The presence of frost in the surface layers contributes to the stability by excluding moisture and avoiding the sharp conductivity changes which normally follow precipitation. The temperature dip in the soil at the end of March was tentatively attributed to the first complete thaw and the resulting percolation of ice water through the soil, but it was not repeated in the following year and may have been partially due to instrument error.

The limiting rate of heat withdrawal for the coil corresponds to 1.00 B.t.u. per hour per linear foot per degree Fahrenheit temperature difference between the coil and the mean annual air (and ground) temperature. This figure by itself has little significance but is quoted here because it has been widely used as a basis for comparison between installations.

The ground temperatures had effectively recovered by the fall of 1950, although the summer was unusually cool and a negligible quantity of heat was returned to the earth during the cooling cycle. This indicates that the performance of this heat pump and coil combination for the test season was representative of the perennial performance to be expected.

HEATING SYSTEM PERFORMANCE AND DESIGN IMPLICATIONS

The quantities necessary for the heat balance were obtained from the electrical and thermal measurements. They were readily calculated from the recorded data except for the quantity of heat extracted from the earth by the ground coil. The latter calculation required an accurate knowledge of the specific heat of the antifreeze solution. A standard denatured alcohol solution was used as the antifreeze base because of its low cost, low viscosity, and noncorrosive properties

when treated. A detailed search of the literature failed to reveal the required specific heat data for either this antifreeze or for straight alcohol at the temperatures encountered in heat pump applications. Hence a separate investigation was undertaken to provide this information. The author wishes to acknowledge his indebtedness to Mr. R. C. Jacobsen who conducted this valuable fundamental investigation. The values obtained, which have a probable error of $\frac{1}{4}\%$, are given in Fig. 8. The data reveal an unforeseen advantage of these solutions because of

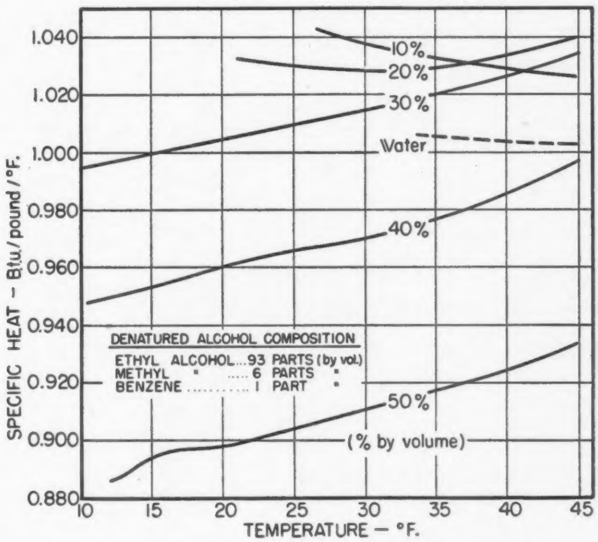


FIG. 8. Specific heat of alcohol antifreeze mixtures.

their exceptionally high specific heats at low concentrations. It is understood that a report on this work will appear separately.

The significant over-all performance figures for the heating season of 1949-50 are shown in Table III. In Fig. 9 the seasonal variations in some of these quantities are indicated.

Because the economic balance is much more critical in heat pump maximum capacity design than it is in conventional fuel burning heater design, particular importance is attached to this aspect of the work. The test season has revealed several significant factors relating to this design problem.

The conventional ASHVE(1) maximum heat-load calculation for the test residence gives a value of 57,600 B.t.u. per hour at design temperatures of −10°F. and 70°F. For the 6869 degree-days experienced, a seasonal heat consumption of 118,800,000 B.t.u. is calculated. The measured consumption was 111,830,000 B.t.u., which is only 6% below the calculated value. Using the degree-day method, the maximum heat load corresponding to this measured

TABLE III

General performance data

Degree-days during heating season	6869
Measured heat supplied	
Heat extracted from ground	50,890,000 B.t.u.
Heat equivalent of input to compressor motor	35,130,000 B.t.u.
Heat equivalent of input to motors of auxiliaries	8,090,000 B.t.u.
Heat equivalent of input to resistance heater	17,710,000 B.t.u.
Total to house	111,820,000 B.t.u.
Electric energy supplied	
Compressor motor	10,181 kwh.
Motors of auxiliaries	2330 kwh.
Resistance heaters	5189 kwh.
Total to heating system	17,700 kwh.
Annual load factor	23%
Maximum electric demand (annual)	9 kw.
Maximum electric demand during utility system peak periods	3 kw.
Seasonal average coefficients of performance	
Over-all including heaters	1.83
Heat pump plus auxiliaries	2.18
Heat pump without auxiliaries	2.47
Compressor motor efficiency	68.5%
Refrigeration compressor cycle efficiency ratio (Freon 12)	0.76
Carnot cycle efficiency ratio	0.56
Average rate of heat withdrawal from ground coil	
Calendar time basis	15.3 B.t.u./hr./linear ft.
Operating time basis	21.9 B.t.u./hr./linear ft.

consumption would be 54,000 B.t.u. per hour. Actually, although daily mean temperatures as low as -5°F. were experienced, with an hourly minimum of -14°F. (see Fig. 12*a*), the heat load never exceeded 44,000 B.t.u. per hour. This load, which is 19% below the apparent maximum of 54,000 B.t.u. per hour, almost equals the installed capacity of the heating system at the coldest time of year. This capacity had been estimated on the premise that minimum temperatures and maximum winds would not coincide, which proved to be the case. The economic advantages of such critical design are reflected in both lower capital investment and lower maximum electric load demand.

The additional allowance for heat load pick-up usually made in fuel burning installations seems to be unwarranted in economic heat pump design. As will be noted from Fig. 12*c*, this deficiency in pick-up capacity sometimes results in the operation of resistance heaters when the average load could be carried by the heat pump alone with better economy. The modulated control could have been adjusted to reduce this effect, but the resulting temperature fluctuations would have been undesirable.

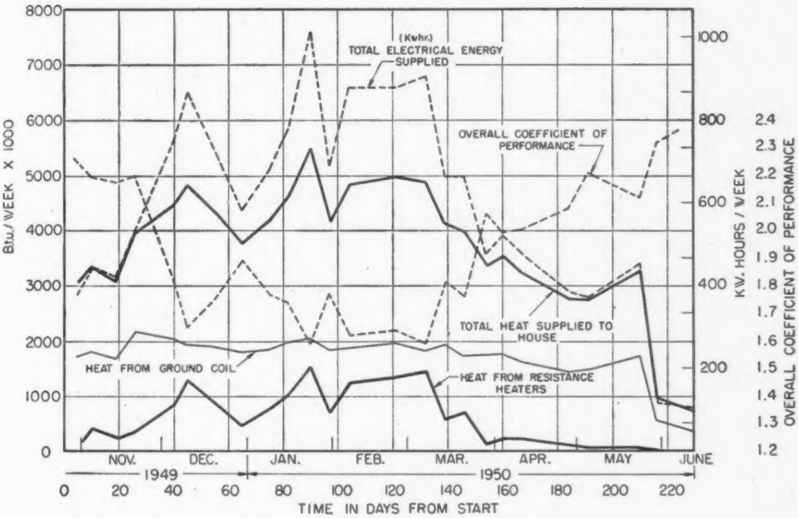


FIG. 9. Seasonal variation in heat balance quantities.

Although the heat pump capacity was sufficient to meet only 53% of the maximum heat demand experienced, it furnished 84% of the total heat supplied over the season. The average annual heat pump capacity is adequate to carry the total house heating load at outdoor design temperatures above 31.6°F. From the actual temperature frequency distribution curve shown in Fig. 10, it

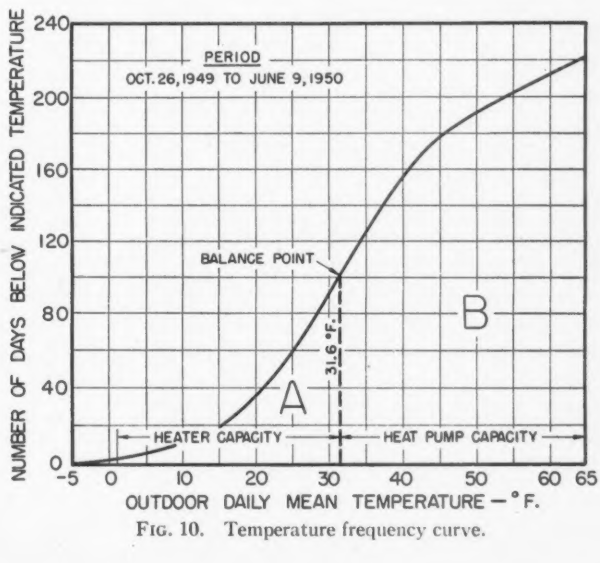


FIG. 10. Temperature frequency curve.

has been found that the ratio of the area A to the total area $A + B$ is 85%. Although the use of daily mean temperatures rather than hourly mean temperatures is not rigidly correct, the close agreement between the observed and the calculated load distribution ratios indicates that such temperature frequency data can be used in design to predict load distribution. Since the load distribution between heat pump and electric heaters determines the over-all coefficient of performance, this distribution is of fundamental importance to the designer. From Fig. 10 it will be seen that a 50% increase in the heat pump capacity will not greatly change the distribution ratio nor will it eliminate the need for auxiliary heaters.

Coefficients of performance can be calculated on several bases. The over-all coefficients used in this report are based on the ratio of the heat supplied to the total heat equivalent of the electric energy used by the heating system. These values are significant with respect to power consumption, but are dependent

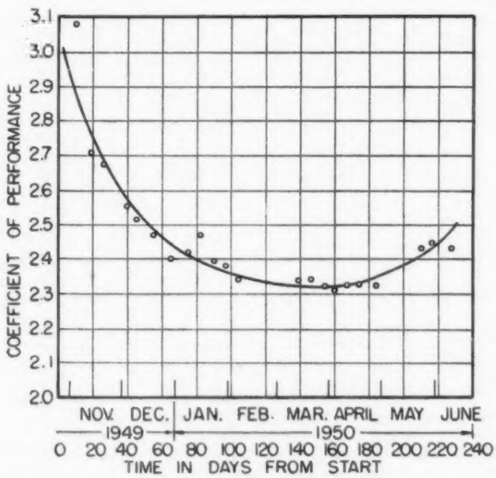


FIG. 11. Seasonal variation in coefficient of performance for heat pump (Compressor-motor unit only).

upon the design distribution between resistance-heater and heat pump capacities. By using the ratio of energy output to energy input for the heat pump alone, a much higher coefficient descriptive of the heat pump performance is obtained. The seasonal variations in these coefficients are shown in Figs. 9 and 11.

The adverse influence of the falling temperature of the ground heat source on the heat pump coefficient of performance can be seen from Fig. 11. This effect, together with the proportionately greater use of the resistance heaters during the coldest months, causes a pronounced reduction in the over-all coefficient of performance, as will be seen from Fig. 9. The electric energy consumption rate curve reflects this behavior, and can be seen to increase more rapidly at this season than does the total heat supply to the house.

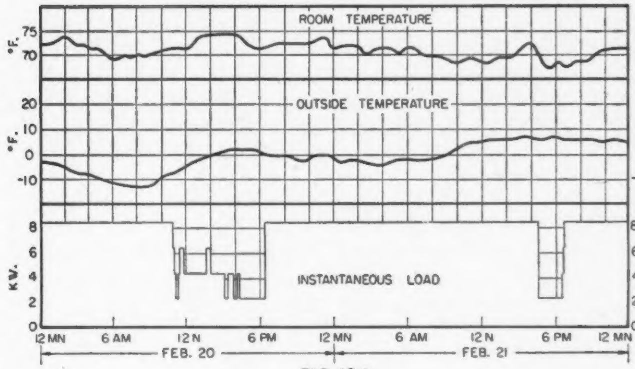


FIG. 12 A

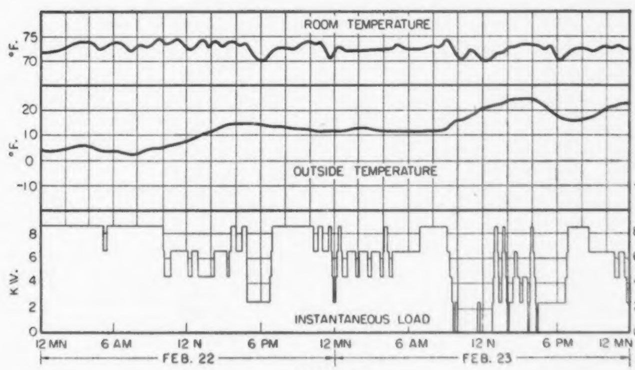


FIG. 12 B

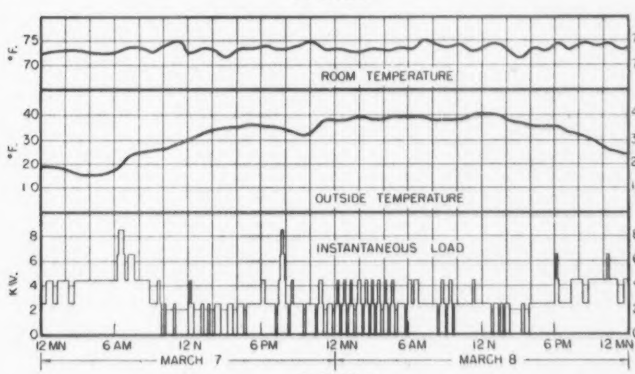


FIG 12 C

FIGS. 12*a*, 12*b*, 12*c*. Typical electric load and temperature records. The demands of the heat pump and of the supplementary 2 kw. resistance heaters are indicated by the steps in the instantaneous load curves. The lowest level is the heat pump demand.

The difference between the "heat supplied to the house" and the "heat from resistance heaters" curves represents the heat supplied by the heat pump. The proportion of the heat supplied which is extracted from the ground can also be seen. Over the heating season, the heat obtained from the ground totalled 50,890,000 B.t.u., which is 45.5% of the total heat supplied to the house and is equivalent to 14,900 kwh. of electric energy.

ELECTRIC LOAD CHARACTERISTICS

Total electric power consumption and other over-all factors relating to the electric load are given in Table III. It will be noted that although the resistance heaters imposed 66% of the maximum demand and consumed 29.5% of the electric power, they supplied only 16% of the seasonal heat requirements.

The annual load factor of 23% has been calculated from the consumption for the heating season only, and would be slightly improved if the summer cooling load were included.

The pattern of the variations in electric power demand for various heat load conditions is shown in Figs. 12*a*, 12*b*, and 12*c*. Fig. 12*a* shows a period including the coldest day (February 20) and also the day of highest heat load (February 21). A period during a more typical cold snap is shown in Fig. 12*b*, and an average winter condition in Fig. 12*c*. The manner in which the heat pump tends to take the base heating load under modulated control can be seen.

Although instantaneous loads are shown, it is apparent that the maximum load indicated will coincide with the integrated maximum demand during several of the colder periods. It should be noted that the heaters were on off-peak control, and the maximum demand never occurred during the hours of the local utility system peak between 4.30 and 6.30 p.m.

The diversity of the load demands on the electric utility system which could be expected from a number of heat pump installations of similar control and design can be inferred from the frequency and duration of the heating cycles. With critical and economic optimum capacity design such as is represented by this installation, it is evident that there will be no diversity between the demands on very cold days (Fig. 12*a*). However, in assessing the effect of heat pump loads on a utility system the load factor and off-peak control feature must be considered as well as the diversity factor.

CONCLUSION

The data given are believed to represent with adequate accuracy the performance of the experimental installation. A sufficiently large body of information was obtained to permit checking of the records and verification of the results.

Thus far the investigation has indicated that ground coils in suitable soils offer a satisfactory heat source in Ontario and that coil design can be undertaken on the steady state heat flow assumption together with field measurements of thermal conductivity.

A ground-coil heat pump system designed to take approximately one-half the maximum heat demand has been shown to supply nearly 85% of the total season's heat requirements. This percentage division appears to be economically favorable where topping heat can be supplied by off-peak power. Other sources of supplementary heat and also heat storage warrant investigation. The results obtained also indicate that critical heat pump capacity design is of economic advantage. A reasonable agreement has been found between design criteria and the observed performance.

The characteristics of the electric load, with the possible exception of diversity factor, appear to be moderately favorable from the utility point of view.

The analysis reported has been made solely on the basis of the technical performance. The economic applicability of the heat pump depends upon the local electrical rate structure and the current capital cost of the equipment. Under the local conditions of this installation an over-all advantage of the heat pump system over other forms of domestic heating is not decisive, unless considerable value is attached to summer cooling and the other attractive features of the heat pump.

REFERENCES

1. American Society of Heating and Ventilating Engineers. Heating, piping and air conditioning guide. Am. Soc. Heating Ventilating Engrs. New York, N.Y. 1950.
2. Hooper, F. C. and Lepper, F. R. Heating, Piping, Air Conditioning, A.S.H.V.E. J. Sect. pp. 129–134. August 1950.

RELAXATION OF TENSION IN STRETCHED DOUGH[1]

By I. Hlynka and J. A. Anderson

ABSTRACT

An apparatus is described for continuous recording of the relaxation process of stretched dough at constant extension. In essence, a motor-driven carriage stretches a ball of dough, impaled on a split-pin holder, to a preset distance, and holds the sample at constant length during the relaxation process. One of the dough stretching pins is connected through a steel spring to a strain gauge; a small displacement of the pin moves an iron slug in the field of a differential transformer, the voltage output of which is coupled to a kymograph by a suitable electronic system. The relaxation of dough under external tension is characterized by a linear relationship between tension and the logarithm of time and may be described by a single parameter, namely the slope of this function. Mathematically, the slope is the product of two variables, the rate of change in tension, and time, i.e. $-K = t\dfrac{dS}{dt}$. Increasing the rest period of the dough increases the slope number of unbromated flour–water doughs. The addition of bromate, however, decreases the slope number with rest period. With increase in either the rate or the amount of extension, the slope number increases at first and then remains at approximately the same value. Increasing absorption or salt concentration has a similar effect in decreasing the slope number. The relaxation curves may also be characterized by the fractional decay time defined as the time required for tension to decay to $1/e$ of its maximum value. In this way, it is shown that the relaxation becomes slower with increasing salt content, and more rapid with increasing water content, even though slope number decreases in both instances. Relaxation of gluten is similar to that of dough, but relaxation of starch paste of doughlike consistency is different. Relaxation of the type studied in this investigation has been reported in the literature to only a limited extent and a satisfactory theoretical basis still remains to be developed.

A study of stress relaxation in stretched dough, held at constant extension, has been undertaken as one aspect of dough rheology. In its practical aspect, stress relaxation is of interest in relation to bread dough properties from the time dough is removed from the mixer, through various stages of handling, and until fermentation stops in the oven. During these various stages of breadmaking, deformations which set up stresses in dough are coupled with the dissipation of stresses through flow and relaxation.

Investigators in this field used both direct (12, 13) and indirect (4, 5, 6, 8, 9, 10, 12) approaches. In the former, viscosity and elastic modulus were usually measured and the Maxwellian relaxation constant was obtained as the viscosity / modulus ratio. In the latter, relaxation was measured directly with a mercury bath extensimeter and with an adapted torsion viscometer. These studies showed that the relaxation phenomena in dough were not simple, either technically or theoretically.

In order to give extended scope to the study of stress relaxation in dough, an apparatus giving a continuous record of the relaxation process directly was

[1] *Manuscript received April 15, 1952.*

Paper No. 119 of the Grain Research Laboratory, Board of Grain Commissioners for Canada, Winnipeg, Manitoba, and No. 298 of the Associate Committee on Grain Research (Canada).

Presented at the Annual Meeting of the Royal Society of Canada, Quebec City. June, 1952

designed. With the aid of this apparatus the relaxation of dough under external tension has been characterized by a linear relationship between tension and the logarithm of time. The influence of varying the amount and rate of extension, resting the dough, absorption, salt concentration, and the addition of bromate have been investigated. It was also possible to examine the relaxation of the two main components of dough, namely gluten and starch. The results obtained in this investigation are presented and discussed.

APPARATUS AND METHOD

A photograph of the "Relaxometer" designed for this study is shown in Fig. 1. It consists essentially of four parts:

(1) A split-pin dough holder on which a ball of dough is impaled and which enables the sample to be placed on the dough stretching pins of the apparatus. An assembled dough holder and its parts are shown in the lower left hand part of Fig. 2.

(2) A motor-driven carriage which stretches the dough a preset distance, then stops and holds the stretched dough sample at constant length during the relaxation process. The carriage is seen on the left in Fig. 2. The rate of travel of the carriage usually employed was 0.8 cm. per second.

(3) A tension gauge to indicate the tension on the dough sample at all times. The right half of Fig. 2 shows the tension gauge. The gauge half of the dough pin is connected through a movable platform to a ring of spring steel, one end of which is fixed. The movable platform also carries a pressed iron slug which moves in the field of a differential transformer. A small movement in the dough pin produces a voltage output in the system proportional to the tension on the ring and thus on the dough. The maximum movement in the dough pin was approximately 1.5 mm.

(4) A kymograph coupled with the output of the differential transformer, in a suitable electronic system, to record graphically the build-up of tension during the stretching process and the decay or dissipation of tension from the time the extension of the dough is stopped until the major part of the stress has been dissipated. The kymograph is designed to take a sheet of ordinary graph paper. The table is mounted on two rails and is motor-driven at the rate of 2 cm. per second. It may be seen at the back in the upper left hand part of Fig. 1.

In operation, 100 gm. of flour is mixed with water for three minutes in a laboratory mixer at an absorption which gives a suitable relaxation curve. The absorption actually used was 54%. The ball of dough is next rounded on the rounder of the Brabender extensograph and impaled onto the assembled and slightly greased dough holder with the aid of a centering extrusion device. The sample is then placed in a humidity controlled chamber for a desired rest period which was usually five minutes.

The sample and its holder are next placed on the dough stretching pin of the relaxometer and the cap holding the parts of the dough holder together is removed. When the switch is closed the dough carriage extends the dough and

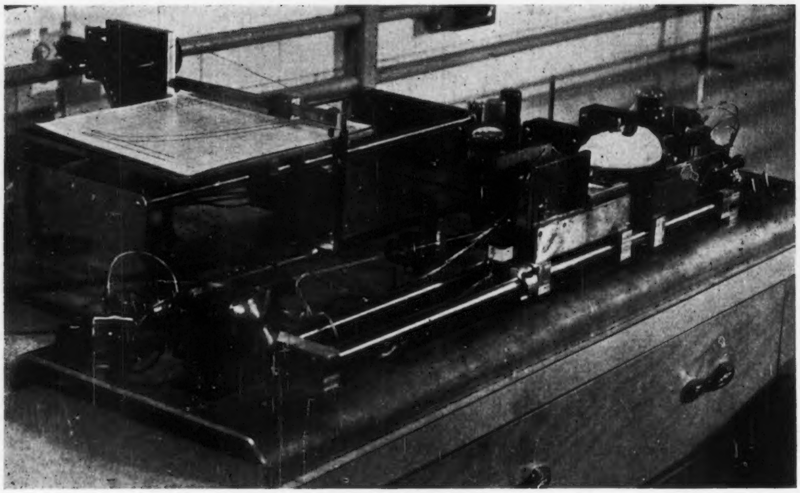


FIG. 1. View of the relaxometer.

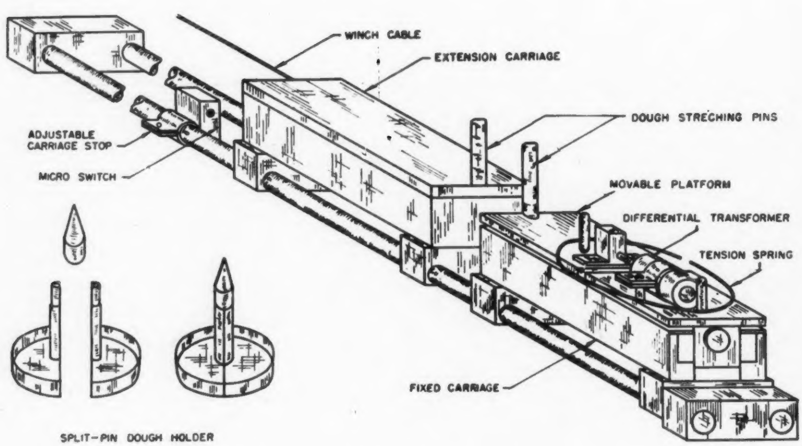


FIG. 2. Essential working parts of the relaxometer.

holds it at a desired extension while the process is being simultaneously recorded. When the record is complete, the switch is turned off, the graph paper is removed, and the apparatus is ready for the next sample.

The flour used was milled to an extraction of approximately 70% from a blend of Canadian hard red spring wheat, two-thirds grading No. 2 Northern and one-third No. 3 Northern. The protein content was 13.0% and the farinograph absorption 62.6% on a 14% moisture basis, but the absorption actually used was 54%.

THE RELAXOGRAM AND ITS PROPERTIES

The curve traced by the relaxometer has been named a "relaxogram." A typical example is shown in the top half of Fig. 3. The ordinate of the curve is

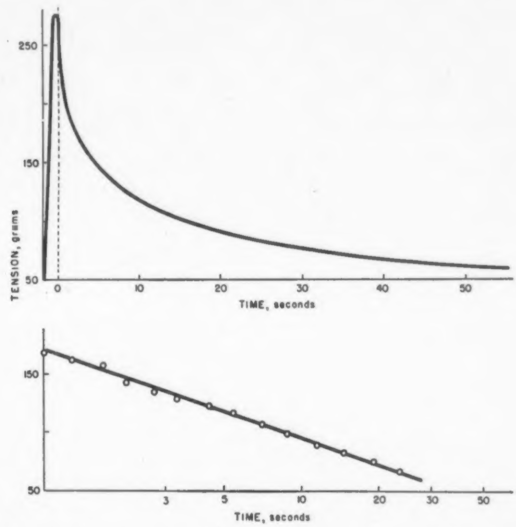


FIG. 3. A relaxogram for dough, above, and its logarithmic time plot.

the tension or load on the sample in grams, and the abscissa is the time in seconds. The relaxation of tension in dough is rapid at first but becomes progressively slower with time. Because the relaxogram forms the basic measurement in the present study, and in addition possesses several interesting features, it merits a brief consideration.

The simplest relaxation known in the literature is the Maxwellian type. It is generally represented as consisting of a viscous and an elastic element in series. The behavior of such a system, called a Maxwell element, can be uniquely specified by a relaxation constant which is the ratio of viscosity to the elastic modulus. Mathematically it is characterized by a linearity between time and the logarithm of stress.

The behavior of dough under external restraint is not Maxwellian. It is thus impossible to determine a unique relaxation constant. One has instead a relaxation "constant" which varies with time and with stress, or as some authors (3) have described it, a spectrum of relaxation times. It is thus meaningless to speak of a unique relaxation constant, modulus of elasticity, or viscosity coefficient for systems of this type. Nevertheless dough possesses a characteristic relaxation function; a linear relationship obtains over the major portion of the range when relaxogram tension is plotted against the logarithm of time. Zero time is taken at the moment dough extension ceases. This linearity is analogous to that observed in rubber and other polymers (1). The lower half of Fig. 3 shows the relaxogram in the upper half plotted on this basis.

The linearity of this relaxation function may be described by

$$S = A - K \log t \tag{1}$$

where S is the tension in grams, A is an appropriate constant, t is time, and K is the slope. If common logarithms are used the value of K must be multiplied by 2.3. The slope is, in effect, a constant which is unique for a given behavior and can be used to define a certain set of properties of the material. As obtained from the relaxation function, the slope is the decrease in tension for one cycle of logarithmic time.

The relaxation function may also be obtained directly from the relaxogram as

$$-K = \frac{dS}{d \log t} \tag{2}$$

which gives

$$-K = t\frac{dS}{dt}. \tag{3}$$

For convenience, the quantity used in this study is not the slope but 1/10th of it, and is referred to as the slope number.

EFFECT OF VARIOUS FACTORS ON RELAXATION

A series of experiments was carried out with the relaxometer to determine the influence of various factors on dough behavior as indicated by the slope number. These experiments will be discussed in subsections which follow.

Rest Period

It is well known that doughs which have been recently handled possess different properties from doughs which have been allowed to rest. This behavior has recently been studied in this laboratory by means of the Brabender extensograph (2). Experiments were therefore made to find out to what extent resting influenced doughs tested on the relaxometer. Doughs were mixed, shaped, and placed on the dough holder in the usual way, and then allowed rest periods varying from 2 to 60 min. before testing. The results are summarized by the top graph in Fig. 4,A where slope number is plotted against rest period. The remaining two graphs in Fig. 4,A will be discussed later in the section on bromate.

The slope number appears to increase with rest period but the increase is only slight. The relaxograms do, however, show differences for doughs rested for various times. Doughs which have been rested for longer times give lower relaxograms in which the tension is dissipated within a shorter time. These

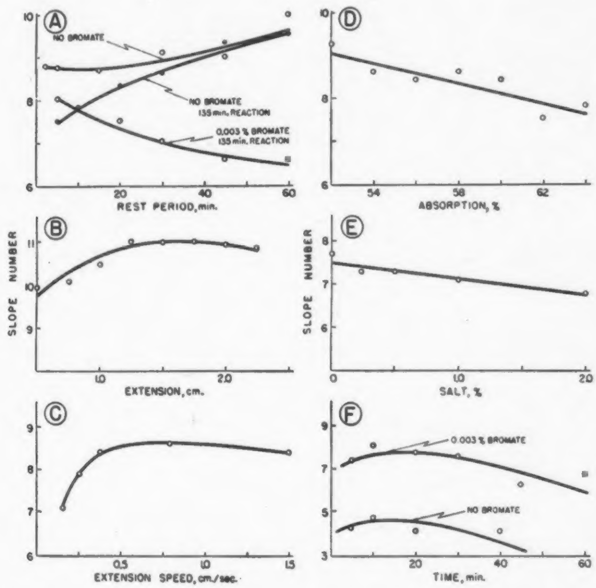


FIG. 4. The influence of various factors on the slope number of doughs and glutens.

changes however are both in the same direction and the slope number does not reflect them. Because a more suitable relaxogram for analysis is obtained at short rest periods, a five minute rest period was adopted throughout most of this investigation.

Extension

The magnitude of extension of the dough sample was varied from 0.50 to 2.25 cm. and slope numbers were obtained for each extension. In all cases the rate of extension was 0.8 cm. per second and relaxograms were obtained at five minutes from the time of placing the sample on the dough holder. The results are summarized in Fig. 4,B. The slope numbers are not those obtained directly from the logarithmic plots of relaxograms but are corrected slope numbers. A word of explanation is therefore required on the origin and significance of the corrected curve.

It has been tacitly assumed that the relaxometer holds the stretched dough sample at constant length. However, the tension gauge indicates tension by a small displacement of one of the pins holding the stretched dough sample. In

dough samples stretched to different extensions this displacement forms a varying fraction of dough extension. A correction is therefore required. The correction formula which is derived from the basic differential equation takes the form of

$$\frac{dS}{dt} = \frac{S}{\tau}\left(\frac{kL - S}{kL + G - S}\right),$$

where S is the tension, τ is the relaxation time, k is the gauge ring constant, L the length of dough, and G is Young's modulus in appropriate units. The term in brackets is the correction factor. The correction to the rate of change of tension is also a correction to the slope number through the identity given in (3),

$$-K = t\frac{dS}{dt}\cdot$$

The correction changes the slope number by an appreciable amount, but has only a negligible influence on the linearity of the logarithmic relaxation curve. In other words, the correction is systematic, and in experiments in which the extension is constant, the uncorrected slopes are entirely comparable. For this reason in all subsequent work no correction has been applied.

Fig. 4,B shows that the slope number increases at first and subsequently remains essentially uninfluenced by varying dough extensions. In the relaxograms, two factors change simultaneously with extension: when doughs are stretched only a short distance, maximum tension, as judged by the height of the relaxogram, is not large. This small tension dissipates within a short time. When doughs are extended greater distances, the height of relaxograms increases, and longer time is required to dissipate the tension. These changes are in such a direction that they are only slightly reflected in the slope number.

Rate of Extension

The influence of the rate of extension on the properties of relaxing doughs was studied next. The magnitude of extension was kept constant at 1.5 cm. and absorption at 54%, but the extension speed was varied from 0.167 to 1.60 cm. per second. Fig. 4,C shows the relation between the rate of dough extension and slope number. As the rate of extension increases the slope number increases to a maximum at an extension speed of about 0.8 cm. per second and remains approximately the same thereafter.

In the relaxogram this is associated mainly with increasing height of relaxograms at the higher rates of extension. Interpretation of the significance of these results will, however, be delayed until the final section of this paper.

Water Content

The effect of varying the water content or absorption of dough on slope number was investigated. The water content of doughs was varied from an absorption of 52 to 64% (14% moisture, flour basis). Dough extension was 1.5 cm. and the rate of extension was 0.8 cm. per second as before. Dough of baking absorption was somewhat too fluid to give good relaxation curves.

Fig. 4,D summaries the results. Over the range of 12%, change in absorption and the effect on the appearance of relaxograms are not especially pronounced. A progressive decrease in slope number is shown with increasing water content of dough. With increasing absorption the relaxogram height decreases rapidly, and the time for tension to dissipate also decreases.

Salt Concentration

Addition of common salt is known to make the doughs stiffer, drier, and less sticky. The influence of salt was therefore included in this study of rheological properties of dough. Doughs were prepared containing salt up to 2.0%. Otherwise the doughs and method of testing were the same as before. Fig. 4,E shows that as the salt content is increased the slope number decreases. This result is what might have been cursorily expected from the known influence of salt on "tightening up" dough. The fact that both salt and water addition to dough had the effect of decreasing slope number will be considered in the final section.

Bromate

The influence of bromate on dough properties is well known. Experiments were designed to study its effect as measured on the relaxometer. Two series of doughs were prepared, one was flour–water doughs, and the other contained 0.003% bromate. Doughs in both series were given 135 min. reaction time to bring out the effect of bromate (2); they were then shaped and placed on the dough holder, and tested at varying times from 2 to 60 min. in the usual way. The two lower curves in Fig. 4,A show the results. The unbromated doughs show an increase in slope number with rest period. These results are similar to those given in the subsection on the effect of rest period, and shown in the top graph. The two series of doughs differ only in that doughs in the present series were allowed a reaction period of 135 min. instead of a zero reaction period, prior to shaping and testing. The doughs which contained 0.003% bromate show a decrease in slope number with rest period, indicating an effect produced by bromate.

Fermentation

An attempt was made to obtain relaxograms on doughs which had been fermented for zero, one, and two hours, then rested for 2 to 60 min. before testing. Consistent results were not obtained and are therefore not presented. However, results in general tended to be more like the bromated than the unbromated doughs.

Type of Flour

It is of practical interest to find out whether the relaxometer can reflect differences in flour quality, or whether it reflects a more general property of dough. Accordingly, relaxograms were obtained on a variety of flours including three samples of hard red spring wheat of good or average milling quality, two lower grades of spring wheat, one from Garnet wheat, and one from amber durum wheat. The data are summarized in Table I. Two absorptions were used, a uniform absorption of 54%, and a constant fraction of the baking absorption.

The relaxograms were very similar except for Garnet which gave quite a stiff dough. In other respects there appeared to be no obvious relation between flour type and slope number. In other words, it is likely that the relaxometer measures a class property of viscoelastic substances, rather than a specific property.

TABLE I

RELAXOGRAM DATA ON VARIOUS FLOURS

Sample No.	Description	Flour protein	Absorption	Slope number	
				54%	Adjusted
1	No. 2, 3	13.0	62.6	7.90	8.56
2	No. 1	12.2	61.0	7.98	7.28
3	No. 1, 2, 3	14.1	64.9	8.28	7.60
4	No. 4	13.4	64.0	7.26	8.34
5	No. 5	12.6	65.6	9.29	8.65
6	Garnet	11.7	64.3	8.00	8.36
7	Durum	10.9	64.4	7.48	7.48

Gluten

The relaxometer lends itself to the study of rheological characteristics not only of dough but of its constituents, gluten and starch. The concluding two subsections describe experiments on gluten and starch.

The rheological properties of gluten are of especial interest because it is generally accepted that rheological properties of dough are largely dependent on its gluten. A series of experiments was designed to explore the more easily determined relaxogram characteristics of gluten. Two series of gluten, analogous to those with dough, were studied. One series contained no bromate and the other approximately 0.003%, wet gluten basis.

The procedure adopted for preparing and handling glutens was as follows. One hundred grams of flour was used for each gluten. The dough was made up, rested, and washed in the conventional way. For bromated doughs, 0.003% bromate was incorporated in the dough and the dough was washed with a solution containing 0.001% bromate. On assay by the Johnson and Alcock procedure (7), the bromated glutens contained about 0.003% bromate, wet gluten basis. All the glutens were then handled at 20° C. until tested. This temperature was selected because glutens kept at room temperature relaxed too rapidly; a temperature of 20° C. gave a relaxogram of the type desired. First, the freshly washed gluten was rested in water for 10 min. at 20° C. to knit together and to mellow. Then it was formed into a ball and allowed to knit together for another 10 min. The gluten was then rounded 20 times on a Brabender rounder, rested for 135 min., rounded again, placed on the sample holder, rested for 5 to 60 min., and stretched. The somewhat more involved procedure for gluten as compared with dough is necessitated by the fact that gluten does not knit immediately when it is formed or shaped, and time must be allowed for this step.

When relaxograms obtained with gluten were plotted as tension vs. logarithmic time, an essentially linear relationship was found, similar to that in doughs. As the rest period was increased the relaxograms were less tall and involved a smaller timescale. Fig. 4,F shows the results for a series of unbromated and bromated glutens in which a reaction period was allowed, before shaping the sample, and the rest period after shaping was varied from 5 to 60 min. Two effects should be noted. First, bromate influences the properties of gluten in such a manner as to increase the slope number. Second, with increasing rest period, the slope number decreases whether the glutens contain bromate or not.

The results on bromated gluten are similar to those on bromated dough. Unbromated glutens have lower slope numbers than corresponding bromated glutens, and show small initial increase followed by a general decrease in slope number with increased rest period. In contrast, unbromated doughs have higher slope numbers than corresponding bromated doughs in the range of rest periods exceeding 60 min. Further, the slope numbers for unbromated doughs increased with increasing rest period. To what the differences between the rheological properties of gluten and dough can be attributed is not at all clear at this time. This remains an interesting subject for further inquiry.

Starch

A heavy starch paste of doughlike consistency is generally described as plastic in contrast to dough or gluten which is considered to be elastic. This distinction is one of degree rather than of kind. Both substances are visco-elastic, and the relaxometer which has been applied to dough and to gluten can also be used in the study of starch.

Two types of starch were studied, purified starch and starch containing the so-called squeegee fraction. These were obtained in the usual way by centrifuging the wash water from doughs, in the former case discarding the top layer of watery dark-colored material, and in the latter, retaining it. The starch was air-dried. The absorption was determined by trial and error to obtain starch "doughs" of suitable consistency to give satisfactory relaxograms. On a 14% moisture basis an absorption of 56% was used for starch, and 80% absorption for starch containing the squeegee fraction. In one set of samples in which the squeegee fraction was prepared separately and then added back to the purified starch, the absorption was only 60%.

The relaxogram of starch paste at 56% absorption is shown in Fig. 5. While the starch relaxogram appears much like dough and gluten relaxograms, the logarithmic time plots are definitely not linear but are concave upward. The behavior of starch is not Maxwellian either, as judged by nonlinearity of logarithmic tension vs. time plots (not shown).

The influence of rest period, and of bromate on starch relaxograms was investigated. Both starch, and starch and squeegee, showed very little influence when their respective "doughs" were tested after resting 5 and 30 min. No effect could be attributed to the action of bromate when starch, and starch and squeegee "doughs", were treated with bromate, allowed a reaction period of

135 min., rounded by hand, and rested for 5 and 25 min. However, in these "doughs" the effect of rest period became definite; the 5 min. relaxograms were considerably higher than the 25 min. ones. The slopes paralleled each other closely.

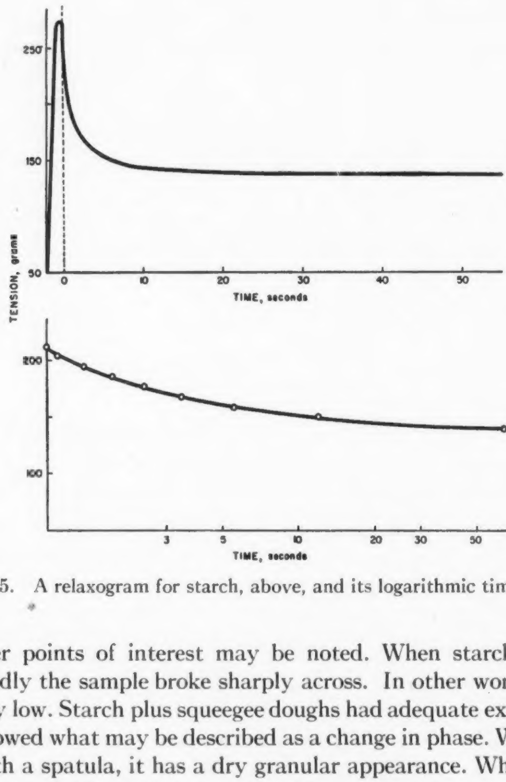


FIG. 5. A relaxogram for starch, above, and its logarithmic time plot.

Two further points of interest may be noted. When starch "dough" was stretched rapidly the sample broke sharply across. In other words, the extensibility was very low. Starch plus squeegee doughs had adequate extensibility. Wet starch also showed what may be described as a change in phase. When wet starch is handled with a spatula, it has a dry granular appearance. When it is allowed to rest it becomes fluid, and has a moist, shiny appearance.

Starch pastes of doughlike consistency thus exhibit rheological behavior which shows differences as well as similarities with the properties of flour doughs. A further study of these will be required for a fuller understanding of dough rheology.

DISCUSSION

The present investigation has re-examined, with the aid of a new apparatus, the relaxation of dough under external stress and has raised a variety of issues. These include the distinction between relaxation of stressed dough and other types of relaxation, the characterization of relaxation of external stress, by a single parameter, the influence of a number of factors on this parameter, and finally the theoretical basis of relaxation. These topics will be discussed briefly.

The relaxometer used in this study records the decay of tension in dough under external restraint. This type of relaxation should be clearly distinguished from the relaxation of internal stresses in unrestrained resting doughs as determined by extensogram properties at periodic intervals. A study of the latter type of relaxation has been recently reported from this laboratory (2). In addition to the manner in which the two types of relaxation are produced, the difference may be further illustrated by the time required for the tension to decay to $1/e$ of its value. In the relaxation of doughs under external stress, the time range is from 2 to 20 sec.; in the relaxation of internal stresses in resting dough, the relaxation time may be from 10 to 100 min. Moreover, in the first type of relaxation, tension is linear with the logarithm of time as has been pointed out in the discussion of relaxogram properties; the second type of relaxation follows the classical Maxwell relationship in which the logarithm of tension is linear with time. It would appear that, in dough, these two relaxations are superposed and the differences which have been pointed out may be conceived as arising from the different portions of the relaxation process that is measured by each of the methods and from the different rheological properties of dough corresponding to the range of the relaxation process involved.

The most important single characteristic of the process of relaxation of doughs under external stress is the linear relationship between stress and logarithmic time. This has already been discussed, in part, in the description of relaxogram properties; the possibility of characterization of dough relaxation in terms of the slope number of the relaxation function was pointed out. Implications of this parameter may now be considered more fully.

The slope constant is a somewhat elusive concept to visualize in terms of a rate process. It does not indicate the rate of stress decay, but, as may be seen by referring again to equation (3), it is the product of rate of change of stress and time. Because it is the product of two components, it may be readily conceived that significant changes in the components may be such that they are not reflected in the slope number. Accordingly, the slope number is not always a sensitive function of a change in dough properties.

Supplementary information to that obtained from slope constants may be obtained from examination of the relaxograms. Both the height of the relaxogram (or initial tension) and some rate factor must be considered in assessing the changes which take place in relaxing dough. On this basis, a quantity which is an index of the rate of decay of tension has been defined. It is called the fractional decay time and is the time taken for tension to decay to $1/e$ of its maximum value. This fraction is selected because it comes in a convenient place on the relaxogram.

The fractional decay time has been examined for each series of relaxograms on which slope number data have been presented. In all instances except one, the fractional decay times merely confirmed the results obtained from slope numbers. The exception is the influence of increasing absorption on slope number. The increase in water content has the same influence on slope number as the increase in salt content; in both instances the slope number decreases. Yet the

addition of water is known to make the dough slacker and the addition of salt has just the opposite effect of tightening the dough. It is in this connection that the concept of fractional decay time shows its usefulness. The fractional decay time increases with increasing salt concentration, indicating that the relaxation becomes slower. But in relaxograms for the increasing absorption series, the fractional decay times decrease, showing that the rate of relaxation actually increases. The anomaly of the decrease in slope number arises from the fact that the relaxogram height decreases faster than the decrease in corresponding fractional time.

The relaxometer also made it possible to do exploratory experiments on the major constituents of dough, namely gluten and starch. Gluten relaxograms are of the same type as those of dough. Starch, however, gave relaxograms which could not be characterized either by a Maxwellian relaxation constant or by the slope number. This investigation was considered as a survey and detailed experiments were not undertaken. Without a doubt, however, detailed studies of these component systems will be necessary in further studies of dough rheology.

Relaxation of the type surveyed in this investigation has been reported to only a limited extent in literature. Andrews, Hofman-Bang, and Tobolsky (1) give an excellent summary of the current status of this type of relaxation, in connection with their studies of polyisobutylene. In addition, a recent attempt to explain the logarithmic time law in the mechanical degradation of dispersions of small particles by Moore and Cravath (11) should be noted. It must be concluded, however, that a satisfactory theoretical basis for relaxation under external tension still remains to be developed, and among the rheological systems to be investigated that of flour–water dough is of considerable interest.

ACKNOWLEDGMENT

The relaxometer was constructed by Mr. H. E. Rasmussen, at the time on the staff of the Grain Research Laboratory. The authors wish to express their indebtedness to him. They also wish to thank Mr. J. R. Cunningham of this Laboratory for his contribution in many discussions of the subject matter in this paper.

REFERENCES

1. Andrews, R. D., Hofman-Bang, N., and Tobolsky, A. V. J. Polymer Sci. 5: 669–692. 1948.
2. Dempster, C. J., Hlynka, I., and Winkler, C. A. Cereal Chem. 29: 39–53. 1952.
3. Doty, P. M. J. Applied Phys. 16: 700–713. 1945.
4. Halton, P. Cereal Chem. 15: 282–294. 1938.
5. Halton, P. Cereal Chem. 26: 24–25. 1949.
6. Halton, P. and Scott-Blair, G. W. Cereal Chem. 14: 201–219. 1937.
7. Johnson, L. R. and Alcock, A. W. Cereal Chem. 25: 266–272. 1948.
8. Kuhn, W., Künzle, O., and Preissman, A. Helv. Chim. Acta. 30: 307–464. 1947.
9. Levi, S. M. Kolloid. Zhur. 10: 112–114. 1948.
10. Levi, S. M. Kolloid. Zhur. 12: 421–426. 1950.
11. Moore, R. J. and Cravath, A. M. Ind. Eng. Chem. 43: 2892–2897. 1951.
12. Schofield, R. K. and Scott-Blair, G. W. Proc. Roy. Soc. (London), A, I, 138: 707–718. 1932; II, 139: 557–566. 1933; III, 141: 72–85. 1933; IV, 160: 87–94. 1937.
13. Volarovich, M. P. and Branopolskaya, R. A. Kolloid. Zhur. 10: 406–412. 1948.

NOTE

The Metallographic Preparation of Porous and Friable Coatings*

During the metallographic examination of the scale layers on heat resistant alloys, great difficulty was experienced in preparing the polished cross sections because of the tendency of the porous and fragile oxide layers to disintegrate during cutting, mounting, grinding, and polishing. The usual method of mounting in plastic by pressure molding not only crushed the layers but did not permit the supporting plastic to enter into the interstices. This resulted in a false representation of the scale structures since, during polishing, soft components were dragged out and any holes were enlarged. Further, it was found to be nearly impossible to polish the specimens free of scratches because chips of scale were continually breaking out and because coarse abrasive was carried along to the later polishing stages by being retained in the numerous pockets in the scale. It was felt that if supporting plastic could be introduced into all the voids in the porous layers, the subsequent grinding and polishing would cause no disintegration of the layers and a true cross section should be obtained. A double vacuum impregnation technique was developed using two liquid plastics which gave satisfactory results.

Plastic Impregnation

The specimen to be impregnated was placed in receiver *B* of the vacuum apparatus shown in Fig. 1 and about 25 ml. of bakelite lacquer put in limb *A* (BL3128 of the Bakelite Company (Canada) Limited was the lacquer used). The liquid plastic was frozen with liquid air and the system evacuated. To assist in the removal of moisture or of adsorbed gas, for certain specimens a small furnace was raised around *B* and the specimen heated while the contaminant was pumped off. The plastic was then allowed to melt and was transferred from *A* to *B* by turning limb *A* upright. The ring seal with drip tip through the 24/40 S.T. joint prevented the plastic from being contaminated by the joint lubricant which would have interfered with the subsequent curing of the plastic. Pumping was continued to remove nearly all the lacquer solvent after which air was admitted, the specimen withdrawn from the plastic, allowed to air-dry for an hour, and baked overnight at 75°C.

After this treatment the bakelite was only partially cured so that when the microspecimens were sawn out with a water-cooled abrasive cut-off wheel the lacquer was not so brittle that it chipped at the cut edge. After cutting, the specimen was heated at 135°C. for 15 min. to complete the cure.

For the second impregnation the microspecimen was replaced in the vacuum apparatus and methyl methacrylate monomer containing 0.2% benzoyl peroxide

**Issued as N.R.C. No. 2777.*

as catalyst was put in limb *A*. As before, the plastic was frozen with liquid air, the system evacuated, the plastic allowed to melt and flow over the specimen by turning limb *A* through 180°. The purpose of this second impregnation was to permit the more fluid monomer to penetrate into the smaller openings exposed at the cut edge which the bakelite lacquer was unable to enter. The receiver *B*

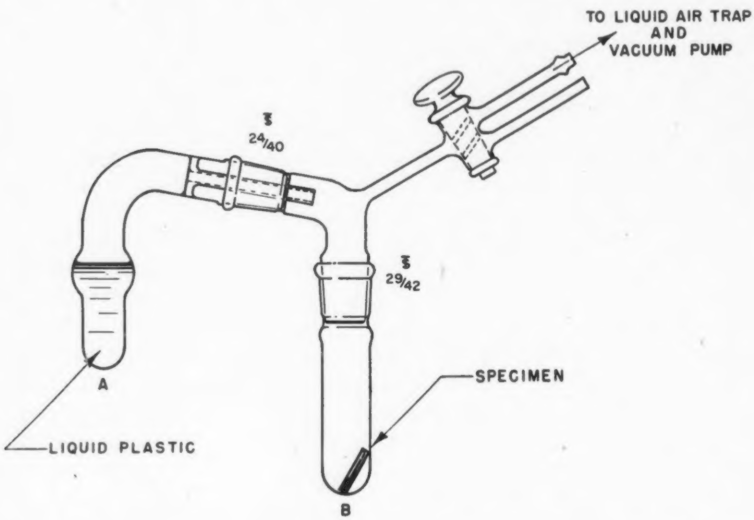


FIG. 1. Diagram of vacuum apparatus for impregnating specimen with liquid plastic.

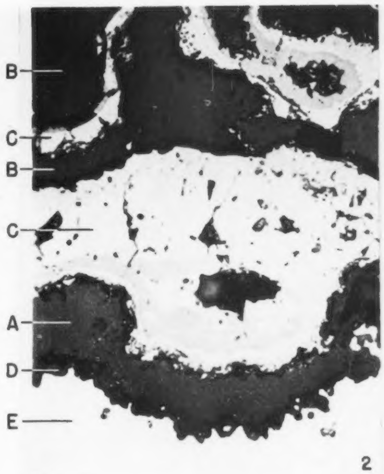
was then removed, fitted with a reflux condenser, and heated at 90°C. until the liquid plastic started to thicken, then held at 60°C. until it had polymerized to a thick viscous liquid. The specimen was then removed from the plastic and maintained at 50°C. overnight. The polymerization was completed by heating for one hour at 75°C. and for 10 min. at 135°C.

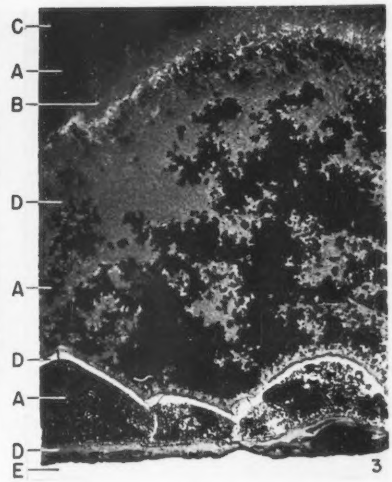
After this double impregnation with liquid plastic the specimen was mounted in molding powder in the usual way and was then ready for grinding and polishing.

Polishing

A second difficulty encountered in the metallographic preparation was edge rounding and relief polishing due to the great difference in hardness between the different materials in the mount, from very hard chromium oxide to very soft silica. Grinding and polishing with silicon carbide and diamond rather than with the softer abrasives gave a well-polished specimen. The mounted specimen was treated as follows:

1. Flattened with a file or coarse abrasive paper or on a belt grinder, care being taken to avoid overheating.





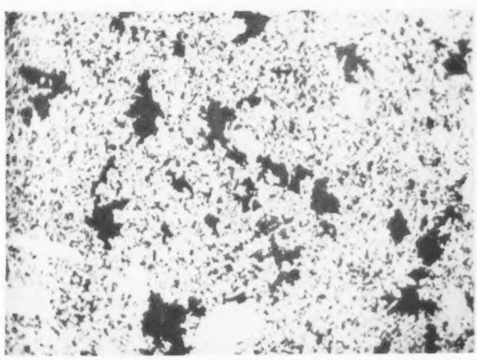


FIG. 2. Section through oxide scale on 27% chromium stainless steel. *A*—methacrylate plastic. *B*—bakelite lacquer. *C*—chromium oxide scale. *D*—silica layer. *E*—metal. Unetched. ×500. (Reduced by three-fifths in reproduction.)

FIG. 3. Section through corrosion product formed on steel in sodium carbonate – potassium chloride solution. *A*—methacrylate plastic. *B*—bakelite lacquer. *C*—bakelite pressure molding plastic. *D*—corrosion product. *E*—metal. Unetched. ×75. (Reduced by three-fifths in reproduction.)

FIG. 4. Section through a rod of activated carbon, showing methacrylate plastic (dark gray) filling the voids in the carbon. Unetched. ×400. (Reduced by three-fifths in reproduction.)

2. Ground on 280, 400, and 600 grit silicon carbite wet-or-dry paper, using water as a lubricant.
3. Ground on 600 grit silicon carbide with graphite as a lubricant.
4. Polished with 2μ diamond abrasive on a lap fitted with a cloth with a short nap using varsol as a lubricant. (Buehler's "Microcloth" proved suitable.)
5. Polished as in (4.) but with 0.5μ diamond.
6. Polished with levigated alumina suspended in water, again on a short-nap cloth.

The result of the impregnation is illustrated in Fig. 2 which is a photomicrograph of a section through the scale formed on a 27% chromium stainless steel by oxidizing in dry air at 2000°F. for 400 hr.

With minor modifications the technique has proved useful for the metallographic preparation of a variety of porous materials. Fig. 3 shows how it has permitted the preparation of a section through the corrosion product adhering to a carbon steel specimen exposed for four months to a solution of $0.05N$ sodium carbonate + $0.05N$ potassium chloride. Fig. 4 demonstrates its use in the metallographic preparation of a rod of activated carbon.

RECEIVED APRIL 2, 1952.
DIVISION OF CHEMISTRY (APPLIED),
NATIONAL RESEARCH COUNCIL OF CANADA,
OTTAWA, CANADA.

D. CAPLAN AND
P. E. BEAUBIEN